PURIFIED PHOSPHORIC ACID PROCESSES

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SUMMARY

One of the fastest growing segments of the fertilizer industry has been the area of liquid mixed fertilizers. Coupled with this growth has been increased emphasis on the quality of the phosphoric acid used for production of liquid mixed fertilizers. Of the two major commerical processes which are presently used for the manufacture of phosphoric acid both have certain disadvantages. Electric furnace grade phosphoric acid is chemically and physically well suited to be used as the source of phosphorus for clear liquid mixed fertilizers but is relatively expensive. Wet process phosphoric acid, on the other hand, is less expensive but when this acid is used, it is virtually impossible to manufacture a clear liquid mixed fertilizer that does not eventually precipitate solids or form a gel due to the impurities present in the acid. Therefore, a potential market exists in the area of clear liquid mixed fertilizer production for a phosphoric acid which is purer than commerical wet process acid but less expensive than commercial electric furnace acid.

The overall objective of this study was to investigate the technical feasibility of producing low impurity, high concentration phosphoric acid by using two chemical routes.

The first process is essentially the one developed by Dr. C.B. Drees (11). This process produces low impurity phosphoric acid by a chemical route which uses the conventional wet process method as a starting point and is based on the dissociation of monocalcium phosphate into phosphoric acid and dicalcium phosphate in the presence of an organic

solvent. Further development of the above process was carried out in which insoluble residue from a dissociation reaction was subjected to repeated treatment with fresh solvents viz., acetone or methanol. The cumulative % P_2O_5 yield in the product phosphoric acid increased with each subsequent treatment through three stages. The maximum conversion was about 90% of theoretical. Higher total yields were obtained with solid than with slurry monocalcium phosphate. The applicability of the process to produce high purity phosphoric acid from low grade phosphate materials was demonstrated by preparation of phosphoric acid from several grades of Florida and North Carolina phosphate rocks, from Florida phosphate slimes, and from Florida phosphate matrix. The compositions and yields of the acids produced were found to be almost identical for all grades of phosphate rock used, and even when phosphate slimes were used the acid produced was of about the same composition except that the Al_2O_3 content was slightly higher. Thus the process was shown to be capable of producing high purity phosphoric acid from waste materials and matrix which were previously found to be uneconomical.

The second process is a modification and simplification of the above phosphoric acid-dicalcium phosphate process in which only phosphoric acid of high concentration can be made directly by a chemical route involving direct digestion of phosphatic materials with sulfuric acid and subsequent extraction of dried acidulate with methanol or acetone.

The approach taken to the experimental phase of the problem for the second process basically involved direct digestion of the phosphate concentrate with sulfuric acid. The acidulated mass was then dried or denned followed by stagewise extraction of phosphoric acid from the

dried acidulate with either methanol or acetone.

Concentration of sulfuric acid used ranged from 93% to 106.75% H_2SO_4 depending on the concentration of phosphoric acid desired. A filterable mass was obtained when the acidulate was dried for 20-60 minutes at 250°C or held in an insulated container for 60 minutes. Three extraction stages with 9 minutes of contact per stage were found to be optimum. The product phosphoric acid from the extraction of dried acidulate, prepared from Florida concentrate I and sulfuric acid of different concentrations, had a concentration between 61 and 70% P_2O_5. The recovery of P_2O_5 from the rock was above 90% except when the rock was digested with sulfuric acid containing 93% H_2SO_4 the yield in that case was much lower.

The process was also shown to be capable of producing phosphoric acid of concentration up to 70% P_2O_5 from low grade phosphatic materials and wastes.

CHAPTER I

INTRODUCTION

General Information and Statement of Problem

Phosphoric acid is an important chemical intermediate, used mainly in the fertilizer field but also in other areas of chemical technology. In fertilizer production it serves as an intermediate between phosphate ore and major end products such as ammonium phosphate, triple superphosphate, liquid mixed fertilizer, high analysis solid mixed fertilizer and some types of nitric phosphate.

There are two basic methods in commerical use for the production of phosphoric acid - the wet process and the furnace process. In the electric furnace process elemental phosphorous is produced by the electrothermic reduction of phosphate rock with carbon (coke). The silica added to the furnace charge behaves as a strong acid at the high temperatures (about 1500°C) employed in furnace operations and combines with the calcium constituent of the phosphate rock to form calcium silicate. The overall reaction, neglecting carbonates, fluorides, and other non-phosphatic constituents, may be expressed as follows:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = P_4 + 6CaSiO_3 + 10CO \qquad (I\text{-}1)$$

In the manufacture of furnace phosphoric acid, the condensed elemental phosphorus is burned in air. The phosphorus oxide vapor (P_4O_{10}) formed reacts with water to produce phosphoric acid.

$$P_4 + 5O_2 = P_4O_{10} \qquad \text{(I-2)}$$

$$P_4O_{10} + 6H_2O = 4H_3PO_4 \qquad \text{(I-3)}$$

The phosphoric acid thus produced has very small amounts of impurities and the major industrial markets for this acid are in the manufacture of sodium phosphates and tetrapotassium pyrophosphate for use in detergents and calcium phosphates for use as an animal feed supplement and in dentifrices, medicinals, glass, food, and plaster stabilizers. An excellent account of the manufacture of phosphoric acid by the electric furnace process is given in Slack (38).

The other way of manufacturing phosphoric acid is by the wet process method. The principal wet process involves digesting phosphate rock (fluorapatite) with sulfuric acid and separating the resulting phosphoric acid from the solid products of the reaction by filtration. The overall reaction with sulfuric acid may be subdivided into three simplified steps.

First, the tricalcium phosphate constituent is converted to phosphoric acid and calcium sulfate.

$$Ca_3(PO_4)_2 + H_2SO_4 = 2H_3PO_4 + 3CaSO_4 \qquad \text{(I-4)}$$

Second, the calcium fluoride constituent of the fluorapatite reacts with sulfuric acid to produce hydrogen fluoride and calcium sulfate.

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4 \qquad \text{(I-5)}$$

Third, the calcium carbonate constituent of the fluorapatite is converted

to carbon dioxide and calcium sulfate.

$$CaCO_3 + H_2SO_4 = CO_2 + CaSO_4 + H_2O \qquad \text{(I-6)}$$

The entire reaction between major constituents and sulfuric acid is as follows:

$$Ca_{10}(PO_4)_6F_2 + CaCO_3 + 11H_2SO_4 = 6H_3PO_4 + 11CaSO_4 + 2HF + H_2O + CO_2 \qquad \text{(I-7)}$$

The hydrogen fluoride produced may react with silica to form silicon tetrafluoride, which then hydrolyzes to fluosilicic acid:

$$4HF + SiO_2 = SiF_4 + 2H_2O \qquad \text{(I-8)}$$

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2 \qquad \text{(I-9)}$$

The calcium sulfate formed in the reactions can be in three stages of hydration: anhydrite, hemihydrate (sometimes called semihydrate), or dihydrate, depending on the reaction temperature and phosphoric acid concentration. A very comprehensive coverage of all the above processes is given in Slack (38) and Noyes (31).

When stoichiometric amounts of reactants, sulfuric acid and acidulation grade phosphate rock, are digested under conditions so as to form calcium sulfate dihydrate, the resultant magma is a mixture of phosphoric acid and gypsum. This mixture is then filtered to obtain phosphoric acid containing approximately 30 percent P_2O_5. This phosphoric acid filtrate is subsequently concentrated to a merchant grade acid containing 54 percent P_2O_5 (around 75 percent H_3PO_4) using vacuum evaporation.

Table 1 gives typical analyses of merchant grade phosphoric acid made from different types of phosphate rock by means of the wet process method (31,38). As can be seen from Table 1, the major impurities in the wet process merchant acid are calcium, iron, aluminum, magnesium, and fluorine. Exclusive usage for wet process phosphoric acid is found in the manufacture of agricultural chemicals.

The rapid growth of liquid fertilizers during the past decade has opened a new field of use for wet process phosphoric acid (1). All the phosphate in liquid fertilizers is supplied by phosphoric acid, which is neutralized with ammonia to form a solution of ammonium phosphate, thus supplying two of the three major plant nutrients, viz., nitrogen and phosphorus.

Wet-process acid is used in liquid fertilizers; however, the iron and aluminum impurities precipitate as an objectionable voluminuous sludge when the acid is ammoniated. Several methods have been used to overcome the sludge formation problem of the clear liquid mixed fertilizer.

One method which has been successfully used to impede the degradation of the clear liquid mixed fertilizer is the use of superphosphoric acid. Superphosphoric acid is a commercial product which contains condensed phosphoric acids such as pyrophosphoric acid and tripolyphosphoric acid and is helpful in avoiding the sludge formation as the polyphosphates in the acid sequesters impurities, holding them in solution.

Electric furnace grade orthophosphoric acid is sometimes used to supply phosphorus to clear liquid mixed fertilizers. However, use of thermal acid, which is roughly twice as expensive as wet acid, poses an economic burden, and is hampered long-term by the fact that output

Table 1. Composition of Typical Commercial Concentrated Wet Process Orthophosphoric Acids (31,38).

Phosphate Rock Source	Acid Composition, Weight Percent									
	P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	SO_4	K_2O	Na_2O	SiO_2
Florida	53.1	0.20	1.32	1.72	0.32	0.5	1.8	0.010	0.30	0.7
	54.8	0.05	0.90	1.10	0.66	0.3	0.7	0.003	0.03	-
	52.1	0.10	1.10	1.10	0.60	0.1	4.8	0.007	0.02	-
	53.1	0.06	1.70	1.23	0.58	0.8	2.6	0.010	0.12	0.7
	55.2	0.04	1.50	1.80	0.58	0.6	0.8	0.007	0.02	-
North Carolina	54.0	0.10	1.00	1.40	1.10	0.7	3.1	-	-	-
Western U.S.	52.7	0.13	1.80	0.40	0.77	0.7	1.9	0.035	0.03	-
	54.2	1.30	1.50	0.70	0.50	1.1	1.2	-	-	0.6
	54.0	0.00	1.89	0.78	0.43	0.2	6.2	0.020	0.21	0.9
	52.6	0.03	2.57	0.96	0.80	0.9	3.1	0.020	0.03	0.8
Tennessee	54.0	0.02	3.90	2.62	-	2.6	2.3	0.020	0.01	0.9

is expected to decline rather than increase.

Yet another method which has been successfully used to prevent the deterioration of clear liquid mixed fertilizer is the usage of conventional wet process phosphoric acid which has been further processed to remove most of the objectionable impurities. A number of chemical processes have been developed which produce a low impurity phosphoric acid by preferentially extracting the acid with an organic solvent while rejecting the undesirable impurities in the raffinate (3,4,5,6,7,14,17, 18,22,28,29,30,32,36,40,41,42). Other papers have described the production of low impurity wet process phosphoric acid using other methods (13,27, 34,35). Slack (38) and Noyes (31) both have good reviews of methods which may be used to purify wet process orthophosphoric acid.

Although considerable effort has been directed toward development of a wet phosphoric acid process, in which strong, relatively pure phosphoric acid can be directly obtained without concentration, no such method has gained widespread commercial acceptance. All the wet acid produced in the United States and most of that produced in the world is manufactured by a relatively weak phosphoric acid process (38); strong acid is obtained by concentration.

The manufacture of phosphoric acid by wet methods has been studied by many investigators, beginning about 1872 (38). One of the most active, the Dorr Co. in the United States, with Krustdunger-Patent Verwertungs A.G., Switzerland, has developed a so-called strong acid process which directly gives a product of about 33% phosphorus pentoxide content. This process has enjoyed commercial acceptance. However, in the last decade or so a couple of important processes have been developed which

are capable of producing a strong wet process acid without concentration (16,18,23,24).

The overall objective of this study was to investigate the technical feasibility of producing low impurity strong phosphoric acid by using two chemical routes. The first process is essentially the one developed by Drees (11) and is used for producing low impurity phosphoric acid by using a certain chemical route which uses the conventional wet process method as a starting point. The proposed chemical process is based on the dissociation of monocalcium phosphate into phosphoric acid and dicalcium phosphate in the presence of an organic solvent according to the following reaction:

$$Ca(H_2PO_4)_2 = H_3PO_4 + CaHPO_4 \qquad (I\text{-}10)$$

A generalized schematic flow diagram showing the major steps involved in this process is shown in Figure 1. The process consists of the following steps:

A. Reaction of phosphatic material*, sulfuric acid and sometimes recycled dicalcium phosphate (DCP) in water to form crude phosphoric acid and gypsum. The principal reaction in this step is:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O = 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF \qquad (I\text{-}11)$$

If dicalcium phosphate is recycled the following reaction also occurs:

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*The term "Phosphatic materials" is used in this dissertation to refer to either phosphate rock, or phosphatic byproducts or phosphate matrix.

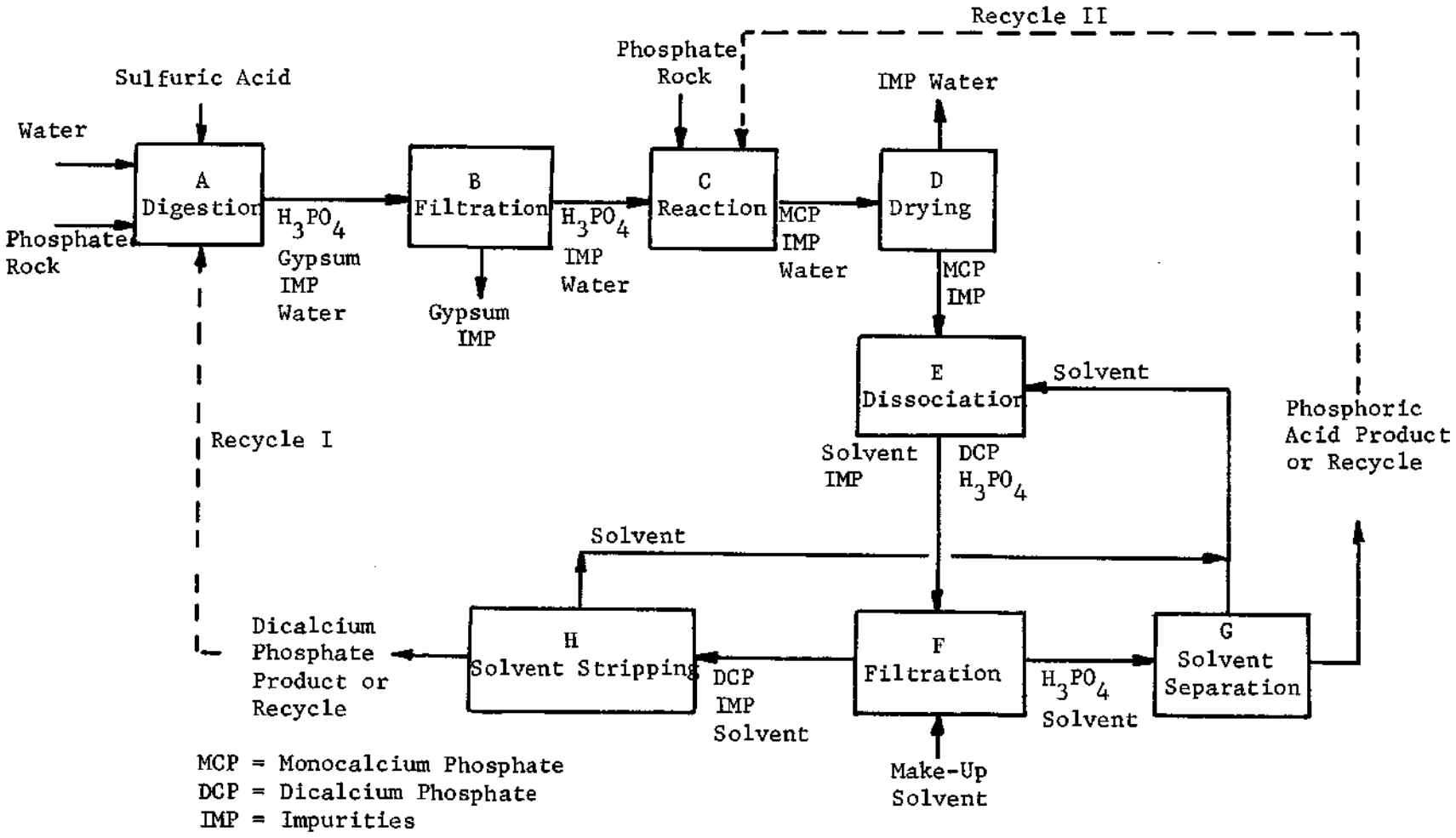

Figure 1. Schematic Diagram for the Dissociation Process

$$CaHPO_4 + H_2SO_4 + 2H_2O = H_3PO_4 + CaSO_4 \cdot 2H_2O \qquad (I\text{-}12)$$

B. Filtration of the digestion products to remove insoluble gypsum and most of the impurities.

C. Reaction of the crude phosphoric acid with phosphatic materials to produce monocalcium phosphate (MCP) according to the following reaction:

$$Ca_{10}(PO_4)_6F_2 + 12\ H_3PO_4 = 9Ca(H_2PO_4)_2 + CaF_2\ . \qquad (I\text{-}13)$$

D. Expulsion of water and some fluorine impurity by drying the monocalcium phosphate slurry. Most of the free water will probably, but not necessarily, be expelled from the monocalcium phosphate slurry during this step.

E. Dissociation of the monocalcium phosphate in the presence of an organic solvent which preferentially dissolves the phosphoric acid but not the dicalcium phosphate which forms, or the impurities present. The chemical reaction occuring at this point is as follows:

$$Ca(H_2PO_4)_2 = H_3PO_4 + CaHPO_4 \qquad (I\text{-}10)$$

F. Filtration of the magma resulting from the dissociation reaction to separate a solution of purified phosphoric acid in the organic solvent from the solid dicalcium phosphate residue containing the impurities. Make-up organic solvent required to off-set losses will probably be best added here as a cake wash.

G. Separation and recovery of the low impurity phosphoric acid product from the solution of acid in organic solvent either by fraction-

ation or extraction. The recovered organic solvent will then be recycled to step E.

H. Stripping of the occluded organic solvent from the dicalcium phosphate residue and subsequent recovery of the stripped solvent for recycle to Step E.

The process up to this point will produce two products, namely, a low impurity phosphoric acid which will be suitable for clear mixed liquid fertilizer production and perhaps many other industrial applications, and impure dicalcium phosphate which can be used as a fertilizer.

In addition, however, the proposed process could be used to produce only one product if desired, namely, either low impurity phosphoric acid or impure dicalcium phosphate. If only low impurity phosphoric acid product were desired, all of the dicalcium phosphate would be recycled back to step A for attack with sulfuric acid as indicated by dotted line I on Figure 1. In this case the dicalcium phosphoric would be converted back to crude phosphoric acid and gypsum and the impurities would be removed from the system in step B along with the gypsum. If only dicalcium phosphate product were desired, the low impurity phosphoric acid would all be recycled to step C as indicated by dotted line II where it would be converted to monocalcium phosphate during reaction with phosphatic materials. It is therefore clear that by the choice of the recycle streams the product from the process could consist of only phosphoric acid, only dicalcium phosphate or any proportion of the two. It is believed that this process will offer the following advantages over other processes for producing a purified wet process acid: production of phosphoric acid of higher purity, higher overall recovery of

low impurity phosphoric acid, and the production of a fertilizer grade dicalcium phosphate, if desired. In addition, it would enable the production of a unit available P_2O_5 with much less mineral acid consumption than by conventional superphosphate and other processes.

The important factors already investigated by Drees (11) are as follows.

Steps A and B. Reaction of phosphate rock, sulfuric acid, and recycled dicalcium phosphate and subsequent filtration of the digestion products. The effect of adding recycled dicalcium phosphate as a reactant in the conventional wet process chemistry and the P_2O_5 recovery from the digestion magma. Also, investigated was the increase of impurities in the crude acid filtrate due to the greater impurity load introduced by recycled dicalcium phosphate.

Steps C, D, E, and F. Production of monocalcium phosphate. Drying of the monocalcium phosphate produced followed by dissociation and filtration. Variables investigated were types of organic solvent, relative proportion of organic solvent and monocalcium phosphate P_2O_5, amount of free water allowed to remain in the monocalcium phosphate P_2O_5, amount of free water allowed to remain in the monocalcium phosphate reactant, reaction time, and reaction temperature. Optimum conditions for steps D, E, and F were also worked out.

Step G. Separation and recovery of the low impurity acid product from organic solvent.

Step H. Solvent stripping from the dicalcium phosphate. The amount of solvent occluded in the wet dicalcium phosphate filter cake

and the chemical analysis of the dried dicalcium phosphate.

The important factors that needed further investigation were as follows:

1. To determine the technical feasibility of producing low impurity orthophosphoric acid and/or fertilizer grade dicalcium phosphate by processing low grade phosphate rocks, and also phosphatic byproducts such as slimes, washings and other rejected phosphatic materials, by a chemical process involving the dissociation of monocalcium phosphate in the presence of an organic solvent. The dissociation process would utilize the general processing steps outlined in the discussion above.

2. To determine the feasibility of using more than one reaction stage for dissociating monocalcium. The filter cake from one dissociation stage would be treated with fresh dissociation solvent to increase the overall phosphoric acid and dicalcium phosphate yield.

The second process investigated in the present work is a modification and simplification of the phosphoric acid/or dicalcium phosphate process in which only high purity phosphoric acid of any desired concentration can be made directly.

A generalised schematic flow diagram showing the major steps involved in the proposed process is shown in Figure 2. The process consists of the following steps:

A. Reaction of phosphatic material with sulfuric acid or fuming sulfuric acid (oleum). The proportion of sulfuric acid or oleum is such as to produce predominantly phosphoric acid and calcium sulfate. The concentration of sulfuric acid or oleum is chosen to produce the desired concentration of phosphoric acid. The principal reaction in this step

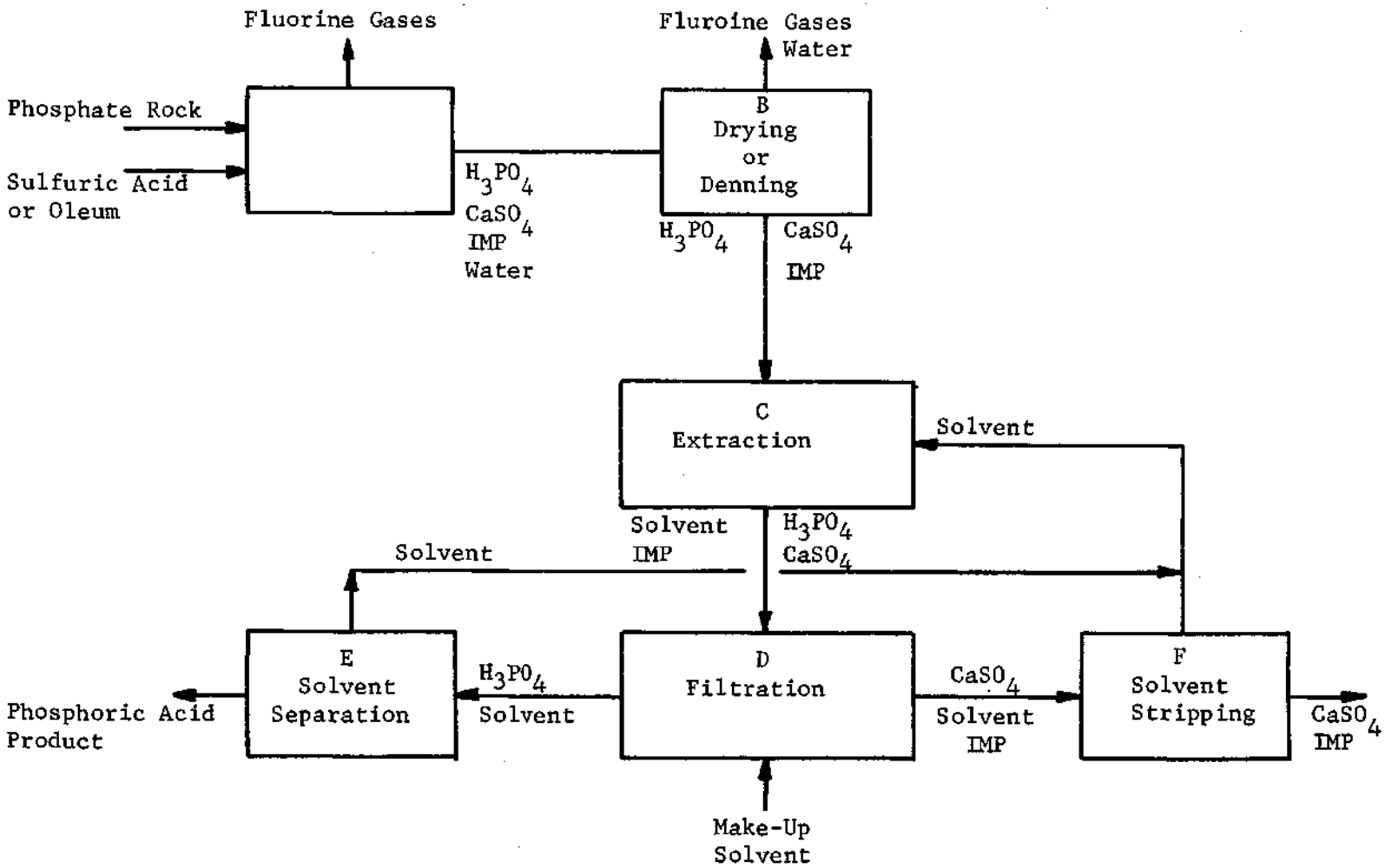

Figure 2. Schematic Diagram for the Direct Acidulation Process

when sulfuric acid is used is:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 = 6H_3PO_4 + 10CaSO_4 + 2HF \qquad (I\text{-}14)$$

If fuming sulfuric acid is used the following reaction also occurs:

$$Ca_{10}(PO_4)_6F_2 + 8H_2SO_4 + 2SO_3 = 2H_3PO_4 + 2H_4P_2O_7 + 10CaSO_4 + 2HF \qquad (I\text{-}15)$$

B. Expulsion of water and some fluorine impurity by drying or denning the digested mass. Most of the free water will probably, but not necessarily, be expelled from the digested mass during this step.

C. Extraction of the dried product with an organic solvent such as methanol or acetone which preferentially dissolves the phosphoric acid but not the calcium sulfate which forms, or the impurities present.

D. Filtration of the mixture to separate a solution or purified phosphoric acid in the organic solvent from the solid calcium sulfate residue containing the impurities. Make-up organic solvent required to off-set losses will probably be best added here as a cake wash.

E. Separation and recovery of the low impurity phosphoric acid product from the solution of acid in organic solvent by fractional distillation. The recovered organic solvent will then be recycled to step C.

F. Stripping of the occluded organic solvent from the calcium sulfate residue and subsequent recovery of the stripped solvent for recycle to Step C.

The process up to this point will produce high purity phosphoric acid of any desired concentration which will be suitable for clear mixed liquid fertilizer production and perhaps many other industrial

applications. Apart from producing clear-liquid mixed fertilizer, this acid can be used for producing triple superphosphate of higher available phosphorus pentoxide when treated with phosphate rock. Due to the low fluorine content, this acid can be used for the manufacture of calcium phosphate for animal food. It is believed that this process will offer the following advantages over other processes for producing a purified wet process acid: strong phosphoric acid of any desired concentration can be produced directly without concentration. Acid of lower strength can also be produced. Total process time using the acidulate filtration procedure is less than 30 minutes, compared to many hours by other wet processes. Fluorine evolution from the rock is almost 90% complete; this makes possible the recovery of a valuable by-product.

The important factors in the proposed process that needed investigation were as follows:

Steps A and B. Reaction of phosphatic material and sulfuric acid and subsequent drying or denning of the digested product. Process parameters to be investigated to obtain easily extractable acidulate include the following: (a) proportion of sulfuric acid and phosphate rock, (b) reaction time and temperature and (c) drying or denning time and temperature.

Step C. The effect of the following variables on the recovery of phosphoric acid from the dried acidulate by solvent extraction: (a) number of extraction stages, (b) contact time of dried or denned acidulate and solvent in each stage, and (c) proportion of organic solvents and phosphate rock P_2O_5. The effect of two organic solvents on the purity

of the acid also needed investigation.

Step D. The effect on the filtration rate due to following variables: (a) amount of free water allowed to remain in the acidulate. (b) type of organic solvent used.

Step E. Separation and recovery of the low impurity acid product from the organic solvent. The product acid needed to be recovered from the organic solvent by either fractionation or extraction in a laboratory simulation step so as to determine the chemical properties of the product acid as well as to determine its visual appearance.

Step F. Solvent stripping from the wet calcium sulfate filter cake needed to be studied.

Literature Survey

It is known that the dissociation of monocalcium phosphate to phosphoric acid and dicalcium phosphate occurs to a limited degree in water. Kharakoz (21) showed that the dissociation of monocalcium phosphate in water proceeds according to an ionic mechanism while Stollenwerk (39) showed that the dissociation proceeds at a unimolecular reaction rate. The conditions under which the dissociation of monocalcium phosphate to phosphoric acid and dicalcium phosphate proceeds in an aqueous system were investigated by Elmore and Farr (12), who found that high concentration and high temperature favored the reaction. The dissociation in the presence of a number of organic solvents, including ethanol, acetone, dioxane, tetrahydrofuran and pyridine, was investigated by Boulle and de Sallier (7), who found that addition of the oxygenated organic compounds caused the monocalcium phosphate to

dissociate into dicalcium phosphate precipitate and phosphoric acid which remained soluble.

A number of studies have been made in the past concerned with the extraction of phosphoric acid by organic solvents and the solubility of phosphoric acid in various organic liquids. A variety of patents exist for chemical processes that produce a purified orthophosphoric acid based on the extraction of crude wet process phosphoric acid by organic solvents with the subsequent recovery of the purified acid product. A very extensive literature review of the papers and patents is given by Drees (11).

A number of investigators have worked on processes in which phosphate rock is treated with strong sulfuric acid or oleum for obtaining a strong, relatively pure phosphoric acid without concentration.

Since 1872 many investigators have studied the manufacture of phosphoric acid by wet methods, the most active among them being Dorr Co. in the United States and Kunstdunger-Patent Verwertungs A.C. in Switzerland (31,38), who developed a so-called strong acid process which directly gives a product of about 33% phosphorus pentoxide content. Nordegren in Sweden produced a strong acid by an anhydrite process (38). Coleman (9,10) developed a wet process for producing phosphoric acid of high concentration and high purity in up to 51% phosphorus pentoxide concentration. Shoeld (37) of the Davison Chemical Co. produced 40 to 42% phosphorus pentoxide acid by treating granulated superphosphate with sulfuric acid and then leaching out the resultant phosphoric acid. In another experiment Litvinenko et al. (26) treated phosphate rock with 75 to 100% sulfuric acid at 140 to 260°C for 20 to 120 min and obtained

a product containing 15 to 17% P_2O_5 of which 94 to 95% was water soluble; 76 to 85% of the fluorine was volatilized. The calcium sulfate in the product was in the anhydrite form. Litvinenko and Isabekora (25) then leached this product with water to obtain phosphoric acid containing 23-24% P_2O_5. Rohac et al. (33) found that when granules of solidified mixture of apatite and 98% H_2SO_4 was coated with a sulfite liquor extract, calcined at 220-300°C and then countercurrently leached with water, a phosphoric acid containing 50% P_2O_5 was obtained in an 89% yield.

The two processes of this type which have received the most attention in the United States are the so-called clinker process developed by the Davison Chemical Division of W.R. Grace and Company, and the fuming sulfuric acid process developed by the Tennessee Valley Authority. Exploratory Laboratory and pilot-plant experiments in the Clinker process are described by Legal et al. (23,24). In the exploratory work, dried phosphate rock containing 30.6 to 33.3% P_2O_5 and ground to minus 80 mesh was treated for about 2 min with 98% technical grade sulfuric acid heated to about 100°C. The product, consisting mainly of stiff particles of about 1/4 to 3/4 in. was then heated for 20-70 min at 200-240°C and was immediately extracted in a countercurrent system consisting of either fixed bed leach columns or filters. Five stages of extraction were needed in the leach column system to obtain a product acid containing 50% P_2O_5. Eight stages of extraction were needed in the filtration system to obtain a product acid containing 47% P_2O_5. In both cases about 95% of the P_2O_5 in the rock was recovered as strong phosphoric acid.

In the clinker process adequate reaction between phosphate rock

and strong (98%) sulfuric acid could be obtained only by heating the acidulate to 200-240°C. Thus it was concluded that use of strong acid would be more attractive if the heating step could be avoided, hence work was started at TVA (16,18) in which fuming sulfuric acid (oleum) was used. In the laboratory work, the phosphate rock was mixed with fuming sulfuric acid for about 1/2 min, into a semigranular solid, which was then denned for 20 min in a dewar flask. The denned acidulate was then countercurrently leached with water to obtain a product containing 50-55% P_2O_5 in an 90-95% yield.

CHAPTER II

EXPERIMENTAL PROCEDURES AND MATERIALS

The equipment and procedures that were employed during the experimental portion of this work are described below.

Preparation of Wet Process Orthophosphoric Acid for Subsequent Preparation of Monocalcium Phosphate

Wet process orthophosphoric acid was prepared for subsequent use by the chemical attack of sulfuric acid on acidulation grade ground phosphate rock from North Carolina or Florida. Wet process orthophosphoric acid was also prepared by chemical digestion with sulfuric acid of ground phosphate rock of any grade or phosphatic by-products or phosphate matrix or dried dicalcium phosphate residues resulting from the previous dissociations of monocalcium phosphate in the presence of an organic solvent. In all preparation of wet process phosphoric acid, conditions were employed such that gypsum or the dihydrate form of calcium sulfate resulted in the reaction slurry.

One to two-gallon batches of wet process phosphoric acid containing around 25 to 30 percent P_2O_5 were made in a 316 stainless steel reaction vessel with a volumetric capacity of around seven gallons. Predetermined amounts of the reactants sulfuric acid, acidulation grade ground phosphate rock, or ground phosphate rock of any grade or phosphatic by-products or phosphate matrix and water as required by the stoichiometry of the wet process phosphoric acid reaction were weighed to the nearest ounce.

Assuming P_2O_5 losses of 3.5 percent due to undigested phosphate rock or phosphatic by-products or phosphate matrix, the amount of technical grade sulfuric acid used was based on the amount of H_2SO_4 required to produce a phosphoric acid containing a residual-free two percent sulfate content after digesting 96.5 percent of the phosphate in the ground phosphatic materials. Wet process acid containing around 25 percent P_2O_5 which had been prepared previously using the same reactants and reaction conditions was also weighed to the nearest ounce using an amount corresponding to 30 weight percent of the total reactor charge. This wet process phosphoric acid was used to dilute the reaction slurry and its use is analogous to the commercial procedure of recycling weak acid from the filter cake wash section of the filters along with some filtered strong acid as a reaction slurry diluent.

The reaction procedure was initiated by adding the water, ground phosphatic raw material and recycled phosphoric acid reactants to the seven gallon reactor while vigorously agitating its contents. Reactor agitation was accomplished by using a variable speed Model 8 stirrer equipped with a two-bladed, five-inch diameter propeller manufactured by the Eastern Industrial Division of LFE. After 15 minutes agitation, the technical grade sulfuric acid was added slowly over a period of one hour while vigorously agitating the reaction vessel contents. In order to prevent the formation of calcium sulfate hemihydrate, the temperature of the reaction slurry was never allowed to rise above 80°C during sulfuric acid agitation. After the addition of sulfuric acid reactant had been completed, the temperature of the vigorously agitated reaction slurry was maintained between 75°C and 80°C by heating with a large hot

plate. In order to insure a high phosphatic raw material digestion efficiency and the growth of easily filterable gypsum crystals, a total digestion period of six hours was allowed from the initial mixing of the phosphatic raw material, water and recycled acid until filtration was started.

The reaction magma was filtered in a 24 centimeter diameter polypropylene filter funnel through Whatman Number 1 filter paper into a four liter pyrex filter flask using water aspiration to provide a vacuum in the filtrate receiver. A volume of reaction magma was filtered such that a gypsum cake thickness of between two and three inches resulted. After filtration of the reaction slurry, the filter funnel and cake were transferred to another four liter pyrex filter flask and the filter cake was washed by adding enough wash water to cover the cake to a depth of about two inches. The resulting filtrate was retained for use as a reaction slurry diluent in subsequent wet process phosphoric acid preparations.

Some wet process orthophosphoric acid prepared from ground phosphatic materials was concentrated to the desired concentration by means of vacuum evaporation for use in subsequent experimentation. Approximately two liters of wet process acid were placed in a three-necked, four liter pyrex boiling flask which was heated with an electrical mantle and which was agitated by a two-bladed propeller driven by an electric motor. A water-cooled glass condenser was connected to the water vapor outlet which eventually discharged the water condensate into a two-necked flask. A vacuum was drawn on the condensate receiver by attaching a connection to a water aspirator. The agitated contents of the boiling flask were

heated to the boiling point after drawing a vacuum on the system. Water evaporation was continued until the volume of water condensate had reached a predetermined level commensurate with the desired final concentration of the phosphoric acid. The concentrated phosphoric acid was subsequently analyzed for various chemical species.

Wet process orthophosphoric acid was manufactured by the sulfuric acid digestion of the dried dicalcium phosphate residues resulting from monocalcium phosphate dissociation reactions in the presence of an organic solvent. Predetermined amounts of technical grade sulfuric acid, ground dicalcium phosphate, and water as required by the stoichiometry of the reaction were weighed to the nearest gram. Assuming P_2O_5 losses of 3.5 percent due to undigested dicalcium phosphate, the amount of technical grade sulfuric acid used was based on the weight of H_2SO_4 required to produce a phosphoric acid containing a residual-free two percent sulfate content after converting 96.5 percent of the phosphate in the ground dicalcium phosphate. Wet process acid containing 25 percent P_2O_5 which had been prepared previously using the same reactants and reaction conditions was also weighed to the nearest gram using an amount corresponding to 25 weight percent of the total reactor charge. This wet process phosphoric acid was used to dilute the reaction slurry so that its solids content was about that of the reaction slurry encountered in commerical wet process acid manufacture.

The reaction procedure was initiated by adding water, ground dicalcium phosphate, and recycled phosphoric acid reactants in a tared 316 stainless steel reaction beaker, while vigorously agitating its content with a propeller type mixer. After 15 minutes agitation, the

technical grade sulfuric acid was added slowly over a period of an additional 15 minutes while vigorously agitating the contents of the beaker. The temperature of the reaction slurry was never allowed to rise above 80°C in order to prevent the formation of calcium sulfate hemihydrate. After completion of the sulfuric acid addition, the temperature of the vigorously agitated reaction slurry was maintained between 75°C and 80°C using a hot plate. In order to insure a high P_2O_5 digestion efficiency and the growth of easily filterable gypsum crystals, a total digestion period of six hours was allowed from the initial mixing of the dicalcium phosphate, water, and recycled acid until slurry filtration was initiated.

The reaction slurry was filtered in a 7 centimeter diameter Buchner filter funnel through Whatman Number 1 filter paper into a 500 milliliter pyrex filter flask using water aspiration to provide a vacuum in the filtrate receiver. The thickness of the resulting filter cake was between one and two inches. After filtration of the reaction slurry, the filter funnel containing the cake was then transferred to another filter flask and the filer cake was washed with enough distilled water to leach the remaining water soluble P_2O_5. The washed gypsum filter cake was oven dried, weighed, and chemically analyzed for P_2O_5 in order to determine the amount of undigested phosphate. The phosphoric acid filtrate was also weighed and chemically analyzed for various chemical species.

Preparation of Monocalcium Phosphate

Batches of monocalcium phosphate were prepared by reacting acidulation grade ground phosphatic raw material from either Florida

or North Carolina with wet process acid containing about 30 percent P_2O_5 which had been previously prepared from ground phosphatic materials from either Florida or North Carolina, respectively. The wet process acid was weighed to the nearest one-tenth gram in a tared 316 stainless steel reaction beaker large enough to contain the monocalcium phosphate slurry product. The phosphoric acid was heated with a hot plate to 80°C while agitating with either a magnetic stirrer or propeller-type mixer. A weighed amount of ground phosphatic material corresponding to that required for the theoretical CaO/P_2O_5 ratio of monocalcium phosphate was then added slowly to the hot agitated acid over a period of 15 minutes in order to minimize foaming and local concentration gradients. The resultant slurry was agitated for two hours total time while maintaining the temperature at 80°C. The resulting monocalcium phosphate slurry was subsequently analyzed for various chemical species.

Monocalcium Phosphate Dissociation Experiments

The dissociation of monocalcium phosphate in the presence of an organic solvent was studied using various amounts of organic solvents and three stages. Three-necked pyrex flasks with capacities ranging from 500 to 5000 milliliters were used for the dissociation studies. A two-bladed propeller and shaft made of 316 stainless steel and driven by an electric motor was inserted in the center neck while the two off-center necks were used for a reflux condenser and sample port. Approximately 100 grams of the monocalcium phosphate reactant were weighed into the flask and the flask was then placed in a water bath which had been pre-set at the desired reaction temperature. A Blue M

Electric Company Model MR-3262A water bath was used with capability of maintaining the bath temperature within $\pm 0.1^{\circ}C$ of a temperature between $0^{\circ}C$ and $90^{\circ}C$. A quantity of organic solvent corresponding to the desired solvent/monocalcium phosphate P_2O_5 ratio was weighed into a flask and the solvent was then heated on a steam bath to the desired reaction temperature. The heated solvent was transferred to the reaction flask and vigorous agitation was started immediately. The agitator was rotated at 425 revolutions per minute as measured by a stroboscopic method. The temperature of the agitated slurry was checked periodially. Samples of the agitated slurry were withdrawn from the flask at various time intervals using a 25 milliliter pipette whose tip had been removed so that any large solid particles in the slurry would not be prevented from being sampled. The sample was immediately filtered through a porous porcelain selas crucible which retained particles larger than nine microns using a water aspirator to pull a vacuum on the filtrate receiver. A filter cake thickness of approximately one inch resulted. After recording the time required for filtration of the slurry to be used for calculation of the filtration rate, the resulting filter cake was washed with a very small amount of ambient temperature solvent used in the reaction. The filter cake was dried at $105^{\circ}C$ and the filtrate was quantitatively transferred to a beaker from which the solvent was evaporated by the use of an infra-red lamp. Both filter cake and filtrate were subsequently analyzed for various chemical species.

In stagewise dissociation, it was necessary to filter the entire content of the flask after the desired reaction time period. At this time, the reaction flask was quickly removed from the water bath and the slurry was filtered in a nine centimeter diameter Buchner funnel through

Whatman Number 42 filter paper while using a water aspirator to provide the vacuum in the filtration flask.

The filter cake from the first and second stages of the stagewise dissociation was oven dried at 105°C for 2 to 3 hours. The powdered residue was then quantiatively transferred to a tared three-necked pyrex flask and reweighed. A quantity of organic solvent corresponding to the desired solvent/m.c.p. P_2O_5 ratio was weighed into a flask and then heated on a steam bath to the desired reaction temperature. The heated solvent was transferred to the reaction flask and vigorous agitation was started immediately. The subsequent details of these experiments parallel exactly the procedure outlined above.

Preparation of Wet Process Phosphoric Acid by Direct Acidulation of Phosphatic Material with Sulfuric Acid.

Wet process phosphoric acid was prepared by the chemical attack of sulfuric acid on acidulation grade ground phosphatic material and subsequently extracted with an organic solvent viz., acetone or methanol. Predetermined amounts of reactants sulfuric acid and acidulation grade ground phosphatic material as required by the stoichiometry for converting all the calcium oxide in the rock to calcium sulfate anhydrite, were weighed to the nearest ounce. Assuming P_2O_5 losses of 3.5 percent due to undigested phosphatic material, the amount of technical grade sulfuric acid used was based on the amount of H_2SO_4 required to produce a phosphoric acid containing a residual-free two percent sulfate content after digesting 96.5 percent of the phosphate in the ground phosphatic material.

The reaction procedure was initiated by adding sulfuric acid, heated to 100°C over a hot plate, to phosphatic material and intimately

mixing together, using a Sears stand mixer model 400.827700 equipped with an automatic 1 to 10 minute timer, for 2 to 3 minutes. At this stage, the mixture formed stiff puttylike particles, about 1/8 to 3/4 inch in size. Fluorine compounds were evolved during the mixing. Temperatures attained during mixing were 200° to 240°C. The mixture was then heated for 20-40 minutes at a temperature of 250°C in a Lindberg Tubular Furnace manufactured by Hevi-Duty Heating Equipment Co. During the heating process fluorine compounds continued to be evolved and the mixture became hard and porous. The dry product or acidulate was then cooled in a dessicator to a temperature of 50°C and then extracted with the desired organic solvent.

Preparation of Wet Process Phosphoric Acid by Direct Acidulation of Phosphatic Material with Fuming Sulfuric Acid

Wet process phosphoric acid was prepared by the chemical attack of fuming sulfuric acid on acidulation grade ground phosphatic material and subsequently extracted with an organic solvent viz., acetone or methanol. Predetermined amount of reactants sulfuric acid and acidulation grade ground phosphatic material, as required by the stoichiometry for converting all the calcium oxide in the rock to calcium sulfate anhydrite, were weighed to the nearest ounce. Assuming P_2O_5 losses of 3.5 percent due to undigested phosphatic material, the amount of technical grade sulfuric acid used was based on the amount of H_2SO_4 required to produce a phosphoric acid containing a residual-free two percent sulfate content after digesting 96.5 percent of the phosphate in the ground phosphatic material.

The reaction procedure was initiated by adding fuming sulfuric acid to phosphatic material and intimately mixing together using a Sears stand mixer model 400.827700 equipped with an automatic 1 to 10 minute timer, for 1 to 2 minutes. At this stage, the mixture formed stiff puttylike particles, about 1/8 to 1/2 inch in size. Fluorine compounds were evolved during the mixing. Temperatures attained during mixing were 240° to 270°C. The resultant acidulate was then held in an insulated container for a period of 20-60 minutes. Temperatures attained during this denning period ranged from 320° to 350°C. The dry product was then cooled in a dessicator to a temperature of 50°C and subjected to size reduction and subsequently extracted with an organic solvent.

Particle Size Reduction of Materials

During the course of this work, it was occasionally necessary to reduce the particle size of some of the solid materials. Substances such as Florida phosphate rock of different grades, dried monocalcium phosphate slurry, phosphatic by-products and dried acidulate resulting from direct acidulation of phosphatic material with sulfuric acid had to be subjected to a particle-size reduction procedure.

Dried monocalcium phosphate was pulverized by hand with a mortar and pestle until the largest particle passed through a U.S. standard 18 mesh screen. The dried acidulate from the direct acidulation process were pulverized by hand with a mortar and pestle until most of the particles passed through U.S. standard 2 mesh screen.

A Mikro sample mill manufactured by the Pulverizing Machinery Company was used to grind the Florida flotation concentrate and phosphatic by-products. The flotation concentrate and phosphatic by-products were

passed repeatedly through the mill until 70 weight percent of the grounded material passed through a 200 mesh U.S. standard screen.

Extraction of Dried Acidulate

The extraction of dried acidulate in the presence of acetone or methanol was studied using various extraction stages, various extraction time periods and different degrees of dryness of the acidulate. A Buchner funnel fitted with Whatman Number 42 filter paper was used to carry out the extraction steps. A Hoffman clamp was used to pinch the polyethylene tube, attached to the stem of the funnel, so that the organic solvent could be held in contact with the acidulate for a period of time.

A known amount of dried acidulate was evenly spread out in the Buchner funnel fitted with Whatman Number 42 filter paper. A quantity of organic solvent corresponding to the desired solvent/rock P_2O_5 ratio was weighed to the nearest ounce and poured in the Buchner funnel. Corresponding to the desired contact period of the solvent with the acidulate the polyethylene tube was pinched. The pinch clip was released after the desired time period and the filtrate collected in the filtration flask. The above procedure was repeated for several stages and the filtrate subsequently analyzed.

Materials

The different materials used in this study are listed below.

Organic Solvents Used for Monocalcium Phosphate Dissociation and Extraction of Dried Acidulate

Methanol. Certified ACS reagent grade absolute methanol from the Fisher Scientific Company.

Table 2. Bulk Price of Commercial Chemical Purchased by Tankcar (8).

Chemicals	Price, Dollars per Pound	Pricing Basis
Methanol	0.051	Freight on Board Gulf Coast Producer
Acetone	0.140	Delivered, Eastern U.S.A.
Sulfuric Acid (93.1% H_2SO_4)	0.022	Delivered, Eastern U.S.A.
Sulfuric Acid (98% H_2SO_4)	0.023	Delivered, Eastern U.S.A.
Oleum (15% free SO_3)	0.025	Delivered, Eastern U.S.A.
Oleum (20% free SO_3)	0.025	Delivered, Eastern U.S.A.
Oleum (30% free SO_3)	0.026	Delivered, Eastern U.S.A.

Acetone. Certified ACS reagent grade acetone from the Fisher Scientific Company.

Phosphatic Raw Materials

Two types of phosphate rock were used in this work. The phosphate rock from Florida was obtained already ground to an acidulation grade. The North Carolina phosphate rock obtained from the Texas Gulf Sulfur Company was a flotation concentrate which was subsequently pulverized to an acidulation grade before using. Both types of rock were dried at 105°C before using.

Four grades of Florida concentrate and one grade of Florida pebble used in this work were obtained from Occidental Chemical Company. The phosphate slime was obtained from the Mobil Chemical Company's slime recovery and beneficiation pilot plant in Clear Springs, Florida. The soft phosphate with colloidal clay (Calphos) was obtained from Thompson Sales Co., Inc. All of the above raw materials were subjected to pulverization to reduce them to acidulation grade before usage in this work. All the materials were also dried at 105°C before using. Chemical composition and particle size distributions of the above materials are given in Tables 3 and 4 respectively.

Wet Process Orthophosphoric Acids

The wet process orthophosphoric acids used in this work were prepared by the acidulation of ground phosphatic materials with sulfuric acid.

Monocalcium Phosphate Materials

Impure monocalcium phosphate containing various amounts of free water were used during the course of this study. All monocalcium phos-

Table 3. Chemical Composition of Experimental Phosphatic Materials

Material Description	Composition, Weight Percent						
	Total P_2O_5	CaO	AL_2O_3	Fe_2O_3	MgO	F	Free Water
Ground Florida Concentrate (I)	34.28	49.50	1.28	1.33	0.25	3.84	0.00
Ground Florida Concentrate (II)	34.02	49.71	1.31	1.43	0.24	-	0.00
Ground Florida Concentrate (III)	33.48	48.17	1.62	1.69	0.26	-	0.00
Ground Florida Concentrate (IV)	33.04	47.88	1.70	1.79	0.32	-	0.00
Ground Florida Concentrate (V)	32.31	45.96	1.82	1.96	0.31	-	0.00
Ground Florida pebble	28.88	41.16	3.26	3.16	0.37	-	0.00
Ground Florida slimes	14.30	18.23	14.78	4.76	-	-	0.00
Ground Florida Phosphate Matrix (I)	20.20	28.89	2.02	0.56	0.17	1.81	0.00
Ground Florida Phosphate Matrix (II)	15.84	21.71	2.51	0.62	0.26	1.90	0.00
Ground Florida Phosphate Matrix (III)	11.57	14.56	8.93	0.96	0.22	0.98	0.00
Ground Florida Phosphate Matrix (IV)	7.53	11.30	3.51	2.27	4.78	1.11	0.00
Ground N. Carolina Concentrate (I)	32.93	54.01	0.80	0.87	0.27	3.99	0.00
Ground N. Carolina Concentrate (II)	30.60	49.10	0.72	0.52	0.22	-	0.00
Soft Phosphate Rock with Colloidal Clay	20.43	27.53	10.46	3.71	0.74	-	0.00

Table 4. Particle Size Distribution of Experimental Phosphatic Materials

Material Description	Cumulative Weight Percentage of Material Retained by U.S. Standard Screen						
	18	20	35	50	60	100	200
Ground Florida Concentrate (I)	-	0.07	0.09	0.36	0.49	2.94	27.13
Ground Florida Concentrate (II)	0.03	0.07	0.17	0.43	0.59	3.73	28.58
Ground Florida Concentrate (III)	0.04	0.09	0.24	0.44	0.73	3.24	28.47
Ground Florida Concentrate (IV)	0.01	0.17	0.32	0.49	0.94	4.87	29.43
Ground Florida Concentrate (V)	0.04	0.21	0.41	0.53	0.84	4.11	30.42
Ground Florida Pebble	0.02	0.19	0.34	0.47	0.91	4.07	29.83
Ground Florida Slimes	-	0.01	0.11	0.34	0.51	2.93	27.10
Ground Florida Phosphate Matrix (I)	-	0.02	0.13	0.31	0.48	3.03	27.73
Ground Florida Phosphate Matrix (II)	-	0.05	0.13	0.49	0.73	3.95	30.41
Ground Florida Phosphate Matrix (III)	-	0.13	0.24	0.58	0.93	3.87	29.42
Ground Florida Phosphate Matrix (IV)	-	0.07	0.12	0.38	0.81	3.63	28.73
Ground N. Carolina Concentrate (I)	-	0.01	0.07	0.19	0.23	0.38	29.57
Ground N. Carolina Concentrate (II)	-	0.00	0.03	0.10	0.13	0.31	30.13
Soft Phosphate Rock with Colloidal Clay	-	0.00	0.00	0.05	0.10	0.17	30.33

phatic materials were initially prepared by reacting ground phosphatic materials from either Florida or North Carolina with wet process phosphoric acid which had been produced using ground phosphatic material from the same region. Portions of this impure monocalcium phosphate slurry were dried so that the resultant monocalcium phosphate material contained from 35.00 to 46.00 weight percent P_2O_5. The dried monocalcium phosphate materials were ground so that the largest particle passed through a U.S. standard 18 mesh screen. The chemical composition and particle size distribution of these monocalcium phosphate materials are shown in Appendix A.

Dried Acidulate Obtained by Direct Acidulation of Phosphatic Material with Sulfuric Acid

Dried acidulate containing various amounts of moisture were used during the course of this study. All the acidulates were initially prepared by reacting acidulation grade ground phosphatic material with different concentrations of sulfuric acid, and subsequently extracting them with an organic solvent. The dried acidulates were ground so that most of the particles passed through a U.S. standard 2 mesh screen. The chemical composition and particle size distribution of these acidulates are shown in Appendix A.

Miscellaneous Chemicals and Materials

Various chemicals and materials that fail to be grouped within any of the aforementioned classifications are listed below.

The sulfuric acid used for digesting ground phosphate rock during the preparation of wet process orthophosphoric acid was technical grade acid obtained from the Fisher Scientific Company.

The acids used in digesting experimental samples in preparation

for chemical analysis and the numerous chemicals used in analyzing these samples for the various chemical species were all reagent grade chemicals obtained from the Fisher Scientific Company, Will Scientific, Inc., or J.T. Baker Chemical Company. These chemicals include buffering reagents, precipitation reagents, indicators and titration reagents.

General Description of the Chemical Analytical Methods

A brief general description of the analytical methods employed for the purpose of analyzing for various chemical species is given here. In almost all cases, analytical methods were used which have been approved and adopted by the Association of Official Agricultural Chemists (20).

Analysis of Phosphorus

There were three types of analysis which were used in this work to determine phosphorus content.

Total Phosphorus. The Association of Official Agricultural Chemists (AOAC) official methods 9 was employed for this analysis (20). This volumetric ammonium molybdate method basically involves digesting the sample in aqua regia followed by the precipitation of the phosphorus in a suitable aliquot using ammonium molybdate as the precipitation reagent. The precipitate is then washed and titrated with standard sodium hydroxide solution to a phenolphthalein end point.

Water Soluble Phosphorus. The AOAC official method 9 was employed for this analysis (20). The method basically involves leaching the water soluble phosphous from a weighed sample of the solid material with distilled water. The water leach is analyzed for phosphorus using the volumetric ammonium molybdate method described above for total

phosphorus.

Citrate Insoluble Phosphorus. The AOAC official method 10 was employed for this analysis (20). The method basically involves dissolving phosphorus from a weighed sample of the solid in hot neutral ammonium citrate solution after removing the water soluble phosphorus. The remaining citrate insoluble phosphorus in the sample is then digested in aqua regia and analyzed for phosphorus using the volumetric ammonium molybdate method described above for total phosphorus.

Analysis for Calcium

The AOAC official method 33 was employed for this analysis (20). This analysis for water soluble calcium basically involves digesting the sample in aqua regia followed by the precipitation of the calcium in a suitable aliquot using ammonium oxalate as the precipitating reagent. The calcium oxalate precipitate is then washed and titrated with standard potassium permanganate solution.

Analysis for Iron, Aluminum, and Magnesium

The AOAC official Atomic absorption spectrophotometry method 29 was employed for these analyses (20). This method of analysis for iron, aluminum, and magnesium basically involves digesting one gram of the sample in hydrochloric acid followed by evaporating the sample to dryness, then subsequently diluting it to appropriate volume with water. Light absorption at appropriate wave lengths was measured with a Beckman 440A atomic absorption spectrophotometer and compared with standard curves.

Analysis of Fluorine

The AOAC official method 9 for fluorine in pesticides was employed

for this analysis (20). This distillation method essentially involves digesting a weighed sample with perchloric acid in a Claisen distilling flask while stripping the evolved hydrogen fluoride with steam. The hydrogen fluoride is absorbed in sodium hydroxide and then titrated with standard thorium nitrate solution.

Analysis for Free Water

The AOAC official method 5 was used for this analysis (20). This vacuum desiccation method essentially involves drying a weighed sample of the solid over anhydrous magnesium perchlorate at ambient temperature under an absolute pressure of nine inches of mercury.

Analysis for Free Water Plus Water of Crystallization

A method developed by Hill and Jacob (19) was used for this analysis. The method basically involves drying a weighed sample for 24 hours at 105°C.

Analysis for Particle Size Distribution

Particle size distributions were determined by using a screening method. The method basically involves screening a weighed sample through a set of standard screens using a successively decreasing grid size. A mechanical device called a Ro-Tap is used to facilitate the passage of sample through the screen openings.

CHAPTER III

EXPERIMENTAL RESULTS AND DISCUSSION

The objective of this study was to investigate the feasibility of using more than one reaction stage for dissociating monocalcium phosphate, and also to further investigate the possibility of manufacturing low impurity phosphoric acid from various grades of phosphate rock and low grade phosphatic by-products and wastes by a route involving the dissociation of monocalcium phosphate in the presence of an organic solvent. A study of modification and simplification of the above phosphoric acid - dicalcium phosphate process was carried out in which only high purity phosphoric acid of any desired concentration can be made directly from various grades of phosphate rock and low grade phosphatic by-products and wastes.

Experimentation for Stagewise Dissociation with Methanol and Acetone Dissociation Solvents

Exploratory experimentation was performed to determine the effect of certain process parameters on the yield of phosphoric acid and impurity rejection from the purified acid product while using the most promising dissociation solvents, methanol and acetone (11), in the stagewise dissociation of monocalcium phosphate prepared from Florida phosphate concentrate. The effect of the following process parameters were investigated: 1) dissociation reaction time in each stage, 2) amount of free water present in the crude monocalcium phosphate reactant and 3) proportion

of organic solvent present during the dissociation in each stage. Near optimum dissociation operating conditions in each stage and the number of stages needed were determined from these studies.

Crude monocalcium phosphate prepared from Florida phosphate concentrate I was used exclusively for these studies in order to eliminate any possible effect on the results which might be attributable to the introduction of raw material variations (phosphate rock source).

It was determined by Drees (11) from a two-way analysis of variance scheme that the parameters of dissociation reaction temperature, solvent/monocalcium phosphate P_2O_5 ratio, and monocalcium phosphate P_2O_5 content had a statistically significant effect on P_2O_5 yield when methanol and acetone were used as dissociation solvents. Dissociation reaction time, however, was not a statistically significant factor and had no effect on product acid P_2O_5 yield at the level investigated for methanol and acetone solvents. The same product acid P_2O_5 yield resulted after four hours of reaction time as was obtained after one hour, and any differences in the data are apparently due to experimental errors alone.

Methanol solvent. The effect of stagewise dissociation on product acid P_2O_5 yield, product acid impurity concentration and filtration rate when methanol was used as dissociation solvent for dissociating monocalcium phosphate containing 32 and 47 percent P_2O_5 are shown in Tables 5 and 6. The product acid P_2O_5 yields, the product acid impurity concentrations and the dissociation slurry filtration rates shown in Tables 5 and 6 are the values obtained after one hour of dissociation reaction period. The detailed results are given in Appendix B.

It has been shown (11) that the product acid P_2O_5 yield increased,

Table 5. Stagewise Dissociation of Crude Monocalcium Phosphate with Methanol at Different Solvent Ratios (The Crude MCP Slurry Prepared from Florida Phosphate Rock contained 32 Percent P_2O_5. Reaction and Filtration Temperature at Each Stage was 55°C).

Number of Stages	Pounds of Methanol per Pound of Total P_2O_5 in Unreacted MCP	Total P_2O_5 Yield in Product Acid[a], Percent	Percent Impurity in Product Acid (Basis 54% P_2O_5)					Filtration Rate, Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
			CaO	Fe_2O_3	AL_2O_3	MgO	Total Major cations	
1	3.16[b,d]	30.90	1.28	0.24	0.22	0.83	2.57	53[c]
1	4.78[b,d]	34.10	0.85	0.10	0.17	0.72	1.84	54[c]
1	6.30[b,d]	33.40	0.67	0.08	0.15	0.70	1.60	26[c]
1	6.30[b]	36.64	0.72	0.08	0.21	0.83	1.84	36[c]
1	12.62[b,d]	38.00	<0.12	0.04	0.14	0.39	<0.69	19[c]
1	24.63[b,d]	35.00	<0.12	0.03	0.29	0.28	<0.72	16[c]
2	6.30;3.98[b]	41.47	0.50	0.10	0.22	0.56	1.38	36;28[c]
2	6.30;4.98[b]	42.14	0.45	0.10	0.19	0.64	1.38	36;28[c]
2	6.30;6.02[b]	42.47	0.39	0.09	0.15	0.59	1.22	36;27[c]
2	6.30;7.06[b]	43.16	0.40	0.08	0.20	0.57	1.25	36;25[c]
2	6.30;8.03[b]	42.85	0.41	0.08	0.20	0.54	1.23	36;25[c]
3	6.30;7.06;4.01[b]	43.25	0.33	0.07	0.16	0.51	1.07	36;25;>29[c]
3	6.30;7.06;5.06[b]	43.48	0.42	0.06	0.16	0.52	1.16	36;25;>28[c]

Table 5. (Continued)

a "P_2O_5 Yield in Product Acid" represents cumulative % P_2O_5 yield in the product phosphoric acid.

b The numbers represent the ratio of methanol/total P_2O_5 in unreacted MCP in each stage.

c The numbers represent the filtration rate for each stage for those experimental runs made using not more than one hour of dissociation reaction time.

d The results obtained by Drees (11) under similar conditions used by the author of this thesis.

Table 6. Stagewise Dissociation of Crude Monocalcium Phosphate with Methanol at Different Solvent Ratios. (The Crude MCP Slurry Prepared from Florida Phosphate Rock contained 47 Percent P_2O_5. Reaction and Filtration Temperature at Each Stage was 55°C).

Number of Stages	Pounds of Methanol per Pound of Total P_2O_5 in Unreacted MCP	Total P_2O_5 Yield in Product Acid[a], Percent	Percent Impurity in Product Acid (Basis 54% P_2O_5)					Filtration Rate, Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
			CaO	Fe_2O_3	AL_2O_3	MgO	Total Major cations	
1	3.11[b,d]	26.10	0.57	0.20	0.28	0.30	1.35	15[c]
1	6.19[b,d]	30.90	0.57	0.05	0.11	0.14	0.87	17[c]
1	6.19[b]	30.71	0.61	0.10	0.07	0.18	0.96	24[c]
1	7.21[b]	34.21	0.58	0.08	0.11	0.13	0.90	24[c]
1	8.17[b]	34.97	0.53	0.09	0.05	0.16	0.83	20[c]
1	9.15[b]	34.54	0.60	0.09	0.08	0.20	0.97	21[c]
2	8.17;4.17[b]	36.97	0.48	0.06	0.11	0.12	0.77	20;17[c]
2	8.17;5.06[b]	39.46	0.54	0.06	0.11	0.16	0.87	20;21[c]
2	8.17;6.12[b]	40.50	0.52	0.08	0.06	0.09	0.75	20;21[c]
2	8.17;7.13[b]	42.42	0.49	0.07	0.06	0.13	0.75	20;22[c]
2	8.17;8.16[b]	43.55	0.50	0.07	0.06	0.15	0.78	20;26[c]
2	8.17;9.14[b]	43.83	0.45	0.07	0.05	0.13	0.70	20;19[c]
2	8.17;10.12[b]	44.00	0.36	0.04	0.06	0.13	0.59	20;20[c]

Table 6. (Continued)

Number of Stages	Pounds of Methanol per Pound of Total P_2O_5 in Unreacted MCP	Total P_2O_5 Yield in Product Acid[a], Percent	Percent Impurity in Product Acid (Basis 54% P_2O_5)					Filtration Rate, Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
			CaO	Fe_2O_3	AL_2O_3	MgO	Total Major cations	
3	8.17;9.14;4.06[b]	44.94	0.42	0.06	0.05	0.12	0.65	20;19;20[c]
3	8.17;9.14;5.12[b]	45.37	0.39	-	-	0.13	>0.52	20;19;26[c]
3	8.17;9.14;6.16[b]	45.41	0.44	-	-	0.09	>0.53	20;19;15[c]

a "P_2O_5 Yield in Product Acid" represents cumulative % P_2O_5 yield in the product phosphoric acid.

b The numbers represent the ratio of methanol/total P_2O_5 in unreacted MCP in each stage.

c The numbers represent the filtration rate for each stage for those experimental runs made using not more than one hour of dissociation reaction time.

d The results obtained by Drees (11) under similar conditions used by the author of this thesis.

the total major cation impurity content of the product acid decreased and the filtration rate of the dissociation slurry increased with increasing dissociation temperature. A high dissociation temperature is also desirable in the continuous process since hot recovered solvent will be recycled to the dissociation stage after having been condensed from the overhead stream of the fractionation stage. It has also been shown (11) that the best dissociation temperatures for methanol and acetone were 55 and 50°C respectively.

The data in Table 5 resulted from experimental runs involving the stagewise dissociation with methanol and crude Florida monocalcium phosphate containing 32 percent P_2O_5 at 55°C using different solvent ratios in each stage. It is seen from Table 5 that the cumulative percent P_2O_5 yield in the product phosphoric acid increases with each subsequent treatment through a total of three stages, although the yield in the third stage is quite small compared to the first two stages. The P_2O_5 yield in product acid resulting from the dissociation of crude Florida monocalcium phosphate containing 32 percent P_2O_5 increased rapidly with increasing solvent/P_2O_5 ratio up to approximately six pounds of methanol per pound of monocalcium phosphate P_2O_5 in the first stage. This increase in P_2O_5 yield is probably caused by an increase in phosphoric acid-solvent association due to the larger proportion of solvent present thus enhancing the monocalcium phosphate dissociation reaction by hindering the reverse reaction. As the ratio was increased above six pounds of methanol per pound of monocalcium phosphate P_2O_5, the product phosphoric acid P_2O_5 yield became relatively constant at approximately 37 percent conversion to product acid P_2O_5 in the first stage, while the cumulative P_2O_5 yield

became relatively constant at 43 percent conversion to product acid P_2O_5 in the second stage after treating crude monocalcium phosphate with six and seven pounds of methanol per pound of P_2O_5 in MCP in successive stages. The maximum conversion was about 87% of the theoretical after treating crude monocalcium phosphate with six, seven and five pounds of methanol per pound of unreacted monocalcium phosphate P_2O_5 in three successive stages.

The data in Table 6 resulted from experimental runs involving the stagewise dissociation with methanol and crude Florida monocalcium phosphate containing 47 percent P_2O_5 at 55°C using different solvent ratios in each stage. The product phosphoric acid yield resulting from the dissociation of crude Florida monocalcium phosphate containing 47 percent P_2O_5 increased as the solvent/P_2O_5 ratio increased, and became quite constant at approximately 35 percent conversion to product acid P_2O_5. Although the product phosphoric acid yield resulting from the dissociation of crude monocalcium phosphate containing 47 percent P_2O_5 was lower than that resulting from dissociation of crude monocalcium phosphate containing 32 percent P_2O_5, the P_2O_5 yield was reasonably high - 31 percent when six pounds of methanol per pound of monocalcium phosphate P_2O_5 was used. Higher total yields were obtained with solid than with slurry monocalcium phosphate.

Tables 5 and 6 also show the total major cation impurity (CaO, Fe_2O_3, Al_2O_3, and MgO) concentration at different methanol solvent/P_2O_5 ratios in the product phosphoric acid resulting from the stagewise dissociation at 55°C of crude Florida monocalcium phosphate containing 32 percent and 47 percent P_2O_5 respectively. The total major cation

impurity concentration in the product phosphoric acid resulting from stagewise dissociation of monocalcium phosphate containing 32 percent and 47 percent P_2O_5 decreased in each stage as the methanol solvent/P_2O_5 ratio was increased. The total major cation impurity concentration in the product phosphoric acid resulting from the dissociation of 32 percent P_2O_5 monocalcium phosphate decreased rapidly up to six pounds of methanol per pound of monocalcium phosphate P_2O_5 after which the decrease was not as pronounced. As can be seen from Tables 5 and 6, the total major cation impurity concentration in product phosphoric acid resulting from the dissociation of 47 percent P_2O_5 monocalcium phosphate was considerably lower than the total major cation impurity concentration in the product phosphoric acid resulting from the dissociation of 32 percent P_2O_5 monocalcium phosphate. This phenomenon probably occured as a result of the lower amount of water in 47 percent P_2O_5 monocalcium phosphate thus allowing only lower amounts of water soluble impurities to be rendered soluble during dissociation.

Tables 5 and 6 also show the filtration rates at different methanol solvent/P_2O_5 ratios of the slurries resulting from the stagewise dissociation at 55°C of crude Florida monocalcium phosphate containing 32 percent and 47 percent P_2O_5. The filtration rates are expressed in terms of pounds of filtrate P_2O_5 that resulted per hour per square foot of filtration area. The filtration rates of the slurries resulting from the stagewise dissociation of 32 percent P_2O_5 monocalcium phosphate decreased as the methanol solvent/ P_2O_5 ratio increased. Even though the filtration rates of the slurries resulting from the stagewise dissociation of 47 percent P_2O_5 monocalcium phosphate were somewhat lower than the filtration rates of the 32 percent

P_2O_5 monocalcium phosphate dissociation slurries, the filtration rates of the 47 percent P_2O_5 monocalcium phosphate dissociation slurries were relatively constant for methanol solvent/P_2O_5 ratios investigated in each stage.

Acetone Solvent. The effect of solvent/P_2O_5 ratio on product acid P_2O_5 yield, product acid impurity concentration and filtration rate when acetone was used as the dissociation solvent in the stagewise dissociation of monocalcium phosphate containing 32 and 47 percent P_2O_5 are shown in Tables 7 and 8 respectively. The product phosphoric acid P_2O_5 yields, the product acid impurity concentrations and the dissociation slurry filtration rates are the values obtained after one hour of dissociation reaction periods in each stage.

The P_2O_5 yield in the product phosphoric acid resulting from the first stage of the stagewise dissociation of crude Florida monocalcium phosphate containing 32 percent P_2O_5, increased with increasing solvent/P_2O_5 ratios up to 6 and then, remained somewhat constant at approximately 30 percent conversion to product acid P_2O_5 with increasing solvent/P_2O_5 ratio from 6.4 to 8.2, while similar results obtained from the dissociation of crude monocalcium phosphate containing 47 percent P_2O_5 show that percent P_2O_5 yield in the product acid increased from 16 to 37 percent with increasing solvent/P_2O_5 ratios from 1.6 to 9.2. It is seen from the results shown in Tables 7 and 8 that the cumulative % P_2O_5 yield in the product phosphoric acid increases with each subsequent treatment through a total of three stages. According to the dissociation reaction, the solid residue from each stage would be correspondingly increased in dicalcium phosphate content and decreased in monocalcium phosphate con-

Table 7. Stagewise Dissociation of Crude Monocalcium Phosphate with Acetone at Different Solvent Ratios. (The Crude MCP Slurry Prepared from Florida Phosphate Rock contained 32 Percent P_2O_5. Reaction and Filtration Temperature at Each Stage was 50°C).

Number of Stages	Pounds of Acetone per Pound of Total P_2O_5 in Unreacted MCP	Total P_2O_5 Yield in Product Acid[a], Percent	Percent Impurity in Product Acid (Basis 54% P_2O_5)					Filtration Rate, Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
			CaO	Fe_2O_3	AL_2O_3	MgO	Total Major cations	
1	6.42[b,d]	29.90	<0.09	0.11	0.22	0.17	<0.59	331[c]
1	6.42[b]	29.59	0.14	0.12	0.29	0.15	0.70	297[c]
1	7.19[b]	29.86	0.14	0.12	0.28	0.15	0.69	307[c]
1	8.16[b]	30.37	0.18	0.13	0.31	0.17	0.79	308[c]
2	8.16;4.22[b]	31.79	0.17	0.12	0.24	0.17	0.70	308;265[c]
2	8.16;5.16[b]	32.74	0.10	0.09	0.34	0.15	0.68	308;260[c]
2	8.16;6.14[b]	33.20	0.12	0.12	0.25	0.19	0.68	308;235[c]
2	8.16;7.18[b]	33.91	0.13	0.14	0.25	0.18	0.70	308;221[c]
2	8.16;8.12[b]	34.48	0.12	0.11	0.19	0.12	0.54	308;206[c]
2	8.16;9.21[b]	34.56	0.12	0.11	0.22	0.15	0.60	308;212[c]
3	8.16;8.12;4.16[b]	35.38	0.08	0.07	0.25	0.16	0.56	308;206;213[c]
3	8.16;8.12;5.21[b]	36.38	0.11	0.11	0.27	0.13	0.62	308;206;184[c]
3	8.16;8.12;6.18[b]	36.88	0.07	0.11	0.26	0.12	0.56	308;206;168[c]

Table 7. (Continued)

Number of Stages	Pounds of Acetone per Pound of Total P_2O_5 in Unreacted MCP	Total P_2O_5 Yield in Product Acid[a], Percent	Percent Impurity in Product Acid (Basis 54% P_2O_5)					Filtration Rate, Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
			CaO	Fe_2O_3	AL_2O_3	MgO	Total Major cations	
3	8.16;8.12;7.18[b]	37.11	0.08	0.11	0.22	0.11	0.52	308;206;144[c]

a "P_2O_5 Yield in Product Acid" represents cumulative % P_2O_5 yield in the product phosphoric acid.

b The numbers represent the ratio of acetone/total P_2O_5 in unreacted MCP in each stage.

c The numbers represent the filtration rate for each stage for those experimental runs made using not more than one hour of dissociation reaction time.

d The results obtained by Drees (11) under similar conditions used by the author of this thesis.

Table 8. Stagewise Dissociation of Crude Monocalcium Phosphate with Acetone at Different Solvent Ratios. (The Crude MCP Slurry Prepared from Florida Phosphate Rock contained 47 Percent P_2O_5. Reaction and Filtration Temperature at Each Stage was 50°C).

Number of Stages	Pounds of Acetone per Pound of Total P_2O_5 in Unreacted MCP	Total P_2O_5 Yield in Product Acid[a], Percent	Percent Impurity in Product Acid (Basis 54% P_2O_5)					Filtration Rate, Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
			CaO	Fe_2O_3	AL_2O_3	MgO	Total Major cations	
1	1.57[b,d]	15.80	0.51	1.38	0.89	0.04	2.82	53[c]
1	3.11[b,d]	19.40	<0.06	0.58	0.51	0.04	<1.19	55[c]
1	4.69[b,d]	29.10	<0.07	0.47	0.48	0.02	<1.04	41[c]
1	6.22[b,d]	30.90	<0.08	0.32	0.32	0.03	<0.75	60[c]
1	6.22[b]	33.35	0.09	0.29	0.49	0.05	0.92	90[c]
1	7.18[b]	34.78	0.09	0.29	0.50	0.08	0.96	89[c]
1	8.19[b]	36.23	0.06	0.34	0.41	0.05	0.86	76[c]
1	9.23[b]	36.59	0.05	0.30	0.43	0.08	0.86	76[c]
2	8.19;4.18[b]	37.77	0.08	0.27	0.35	0.05	0.75	86;73[c]
2	8.19;5.21[b]	39.30	0.05	0.32	0.26	0.05	0.68	86;66[c]
2	8.19;6.18[b]	40.45	<0.05	0.33	0.28	<0.05	<0.71	86;72[c]
2	8.19;7.21[b]	42.05	0.06	0.23	0.33	<0.05	<0.67	86;61[c]
2	8.19;8.15[b]	43.21	<0.05	0.29	0.30	<0.05	<0.69	86;61[c]

Table 8. (Continued)

Number of Stages	Pounds of Acetone per Pound of Total P_2O_5 in Unreacted MCP	Total P_2O_5 Yield in Product Acid[a], Percent	Percent Impurity in Product Acid (Basis 54% P_2O_5)					Filtration Rate, Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
			CaO	Fe_2O_3	AL_2O_3	MgO	Total Major cations	
2	8.19;9.21[b]	44.18	0.05	0.26	0.39	<0.05	<0.75	86;59[c]
2	8.19;10.12[b]	44.44	0.05	0.27	0.27	0.05	0.64	86;52[c]
2	8.19;11.22[b]	44.57	-	0.24	0.37	0.06	>0.67	86;43[c]
3	8.19;10.12;4.18[b]	45.01	0.05	0.20	0.31	0.05	0.61	86;52;36[c]
3	8.19;10.12;5.12[b]	45.67	-	0.25	0.28	0.06	>0.59	86;52;32[c]
3	8.19;10.12;6.21[b]	46.13	0.05	0.26	0.30	0.06	0.67	86;52;27[c]

a "P_2O_5 Yield in Product Acid" represents cumulative % P_2O_5 yield in the product phosphoric acid.

b The numbers represent the ratio of acetone/total P_2O_5 in unreacted MCP in each stage.

c The numbers represent the filtration rate for each stage for those experimental runs made using not more than one hour of dissociation reaction time.

d The results obtained by Drees (11) under similar conditions used by the author of this thesis.

tent. The maximum conversion was about 90% of theoretical. Higher total yields were obtained with solid than with slurry monocalcium phosphate.

Tables 7 and 8 also show the total major cation impurity (CaO, Fe_2O_3, Al_2O_3, and MgO) concentrations at different acetone solvent/P_2O_5 ratios in the product phosphoric acid resulting from the stagewise dissociation at 50°C of crude Florida monocalcium phosphate containing 32 and 47 percent P_2O_5 respectively. As can be seen from Tables 7 and 8, the total major cation impurity concentration in the product phosphoric acid decreased with each subsequent treatment through a total of three stages. The total major cation impurity concentration in the product phosphoric acid decreased rapidly as the solvent/P_2O_5 ratio was increased with 1.6 to 3.1 pounds of acetone per pound of monocalcium phosphate P_2O_5 in the first stage of the stagewise dissociation of monocalcium phosphate containing 47 percent P_2O_5. However, above a ratio of 3.1 pounds of acetone per pound of monocalcium phosphate P_2O_5, the total major cation impurity concentration in the product phosphoric acid was relatively constant at approximately one percent.

When the data concerned with the product acid impurity concentrations when using methanol solvent (see Tables 5 and 6) are compared with those when using acetone solvent (see Tables 7 and 8), it can be seen that the choice of solvent dictated which major cation impurities were preferentially rejected from the product phosphoric acid. When methanol was used as the dissociation solvent, the concentrations of Fe_2O_3 and Al_2O_3 in the product phosphoric acid were generally much lower than when acetone was the dissociation solvent. However, when acetone was used as

the dissociation solvent, the concentrations of CaO and MgO were generally much lower than when methanol was the dissociation solvent. This preferential rejection of impurities can be attributed to difference in solubility of different impurities in two solvents. However, even though methanol rejects iron and aluminum impurities better than acetone and acetone rejects calcium and magnesium impurities better than methanol, the total major cation impurity concentration in the product phosphoric acid is approximately the same when dissociating with methanol or acetone using similar reaction conditions the only exception is when monocalcium phosphate containing 32 percent P_2O_5 was dissociated with methanol. This irregularity can be attributed to the lower ratio of solvent/P_2O_5 in monocalcium phosphate being used in each stage.

Tables 7 and 8, also show the filtration rates at different acetone solvent/P_2O_5 ratios of the slurries resulting from the dissociation at 50°C of crude Florida monocalcium phosphate containing 32 and 47 percent P_2O_5 respectively. The filtration rates are expressed in terms of pounds of filtrate P_2O_5 that resulted per hour per square foot of filtration area. It can be seen from the above two tables that the dissociation slurry filtration rates decrease with each subsequent treatment through a total of three stages.

When the data on dissociation slurry filtration rates with methanol solvent (see Table 9) are compared with those with acetone solvent, it can be discerned that use of acetone solvent resulted in higher dissociation slurry filtration rates than when methanol was used as solvent. This difference in filtration rates can be attributed to the fact that acetone has lower viscosity than methanol.

Table 9. Stagewise Dissociation of Crude Monocalcium Phosphate with Either Acetone or Methanol at Optimum Solvent Ratios in Each Stage. (The Crude MCP Slurry Prepared from Florida Phosphate Rock Contained Either 32 or 47 Percent P_2O_5).

Type of Solvent	Number of Stages	Reaction and Filtration Temperature °C	Optimum Ratio of Solvent/P_2O_5 in MCP in in Each Stage		Total P_2O_5 Yield in Product Acid[a], Percent		Filtration Rate[b], lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area		Filtration Rate[b], Gallons of Filtrate/Hr/Sq Ft of Filtration Area	
			32% P_2O_5 in MCP	47% P_2O_5 in MCP	32% P_2O_5 in MCP	47% P_2O_5 in MCP	32% P_2O_5 in MCP	47% P_2O_5 in MCP	32% P_2O_5 in MCP	47% P_2O_5 in MCP
Methanol	1	55	6.30	8.17	36.64	34.97	36	20	93	70
Methanol	2	55	7.06	9.14	43.16	43.83	36;25	20;19	93;406	70;294
Methanol	3	55	5.06	6.16	43.48	45.41	36;25;>28	20;19;15	93;406;>5000	70;294;834
Acetone	1	50	8.16	8.19	30.37	36.23	308	86	1271	299
Acetone	2	50	8.12	10.12	34.48	44.44	308;206	86;52	1271;6250	299;985
Acetone	3	50	6.18	6.21	36.88	46.13	308;206 168	86;52 27	1271;6250;6650	299;985;1524

a "P_2O_5 Yield in Product Acid" represents cumulative % P_2O_5 yield in the product phosphoric acid.

b "Filtration Rate" represents the values obtained after one hour of dissociation reaction time period.

Dissociation of Monocalcium Phosphate Prepared from Various Phosphatic Materials with Methanol and Acetone

A number of exploratory experimental runs were made to investigate the dissociation of crude monocalcium phosphate prepared from various phosphatic by-products in the presence of acetone and methanol solvents. The data resulting from these experiments were used to evaluate the feasibility of using this process for the manufacture of low impurity phosphoric acid from the dissociation of crude monocalcium phosphate prepared from various grades of phosphatic materials.

Condensed data which resulted from these exploratory experimental runs are presented in Table 10. The detailed results are given in Appendix C. Table 10 shows the P_2O_5 yield in the product phosphoric acid, the major cation impurities in product phosphoric acid containing 54 percent P_2O_5 along with the filtration rate of the dissociation slurry which resulted from the dissociation with methanol and acetone of crude monocalcium phosphate prepared from various phosphatic materials. The table also shows the types of phosphatic materials, the type of dissociation solvent, and the total percent P_2O_5 in unreacted monocalcium phosphate. Reaction and filtration temperatures for acetone and methanol were 50°C and 55°C respectively. A nearly constant ratio of approximately 6.2 pounds of solvent per pound of total P_2O_5 in the unreacted monocalcium phosphate was used for these experiments. The crude monocalcium phosphates used for these experiments were solid materials which had to be pulverized prior to dissociation.

The P_2O_5 yields which appear in Table 10 represent the percentage

Table 10. Dissociation of Crude Monocalcium Phosphate with 6 Pounds of Solvent/Pound of Unreacted P_2O_5 in MCP. (The Crude MCP were Prepared from Various Grades of Phosphatic Materials. Reaction and Filtration Temperatures for Acetone and Methanol were 50°C and 55°C Respectively).

Raw Materials (% P_2O_5)	Solvent	Percent Total P_2O_5 in Unreacted MCP	P_2O_5 Yield in Product Acid[a], Percent	Percent Impurity in Product Acid (Basis 54 Percent P_2O_5[a])					Filtration Rate[a], lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	Total Major cations	
Florida Concentrate I (34.3)	Methanol	47.00	30.71	0.61	0.10	0.07	0.18	0.96	24
	Acetone	47.00	32.93	0.09	0.29	0.49	0.05	0.92	90
Florida Concentrate II (34.0)	Methanol	46.40	28.52	0.48	0.07	0.14	0.20	0.89	34
	Acetone	46.40	29.89	0.05	0.47	0.49	0.14	1.15	77
Florida Concentrate III (33.5)	Methanol	45.30	28.37	0.45	0.13	0.07	0.32	0.97	30
	Acetone	45.30	29.78	0.07	0.39	0.50	0.08	1.04	52
Florida Concentrate IV (33.0)	Methanol	44.60	28.21	0.49	0.07	0.09	0.25	0.90	21
	Acetone	44.60	29.40	0.07	0.35	0.48	0.06	0.96	65
Florida Concentrate V (32.3)	Methanol	45.40	28.04	0.51	0.06	0.10	0.24	0.91	19
	Acetone	45.40	30.54	0.09	0.47	0.39	0.04	0.99	51
Florida Pebble (28.9)	Methanol	44.80	28.22	0.44	0.15	0.17	0.35	1.11	19
	Acetone	44.80	29.14	0.11	0.63	0.57	0.06	1.37	48
Florida Matrix I (20.2)	Methanol	42.10	27.23	0.54	0.16	0.12	0.69	1.51	11
	Acetone	42.10	29.41	0.09	0.28	0.36	0.06	0.79	56

Table 10. (Continued)

Raw Materials (% P_2O_5)	Solvent	Percent Total P_2O_5 in Unreacted MCP	P_2O_5 Yield in Product Acid[a], Percent	Percent Impurity in Product Acid (Basis 54 Percent P_2O_5[a])					Filtration Rate[a], lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	Total Major cations	
Florida Matrix II (15.8)	Methanol	40.20	26.87	0.60	0.23	0.16	0.61	1.60	9
	Acetone	40.20	28.88	0.09	0.29	0.32	0.06	0.76	33
Florida Matrix III (11.6)	Methanol	40.63	27.42	0.51	0.42	0.43	0.77	2.13	9
	Acetone	40.63	28.17	0.10	0.34	0.70	0.08	1.22	28
Florida Matrix IV (7.5)	Methanol	38.71	26.28	0.63	0.41	0.25	0.53	1.82	8
	Acetone	38.71	28.54	0.07	0.39	0.27	0.11	0.84	27
Soft Phosphate Rock with Colloidal Clay (20.4)	Methanol	41.63	27.40	0.82	0.33	0.48	0.28	1.91	9
	Acetone	41.63	28.73	0.15	0.42	0.48	0.09	1.14	25
Florida Slimes (14.30)	Methanol	41.20	28.08	0.51	0.19	0.93	0.50	2.13	10
	Acetone	41.20	30.59	0.07	0.61	1.41	0.05	2.14	61
N. Carolina Concentrate I (32.9)	Methanol	46.20	31.91	0.66	0.12	0.23	0.57	1.58	24
	Acetone	46.20	32.53	0.04	0.63	0.32	0.10	1.09	90
N. Carolina Concentrate II (30.6)	Methanol	45.67	30.85	0.64	0.11	0.07	0.11	0.93	21
	Acetone	45.67	31.57	0.09	0.29	0.31	0.06	0.75	80

a "P_2O_5 Yield", "Percent Impurity" and "Filtration Rate" represents the values after one hour of dissociation reaction time period.

of monocalcium phosphate reactant P_2O_5 that resulted as product phosphoric acid P_2O_5 after one hour of dissociation reaction period investigated using a certain set of reaction conditions. The concentrations of major cation impurities (CaO, Fe_2O_3, Al_2O_3, MgO and total major cations) that appear in Table 10 represent the weight percentage of these species in product phosphoric acid containing 54 percent P_2O_5 with all such impurity concentrations having been obtained after one hour of dissociation period investigated using a certain set of reaction conditions. The total major cation impurity concentration in product phosphoric acid is the sum of the impurity concentrations of the CaO, Fe_2O_3, Al_2O_3, and MgO species. The filtration rates appearing in Table 10 represent the rate of filtration of dissociation slurry after one hour of dissociation reaction period.

From the results given in Table 10 it may be seen that the P_2O_5 yields of the acids produced varied from 32.93 percent to 28.17 percent when monocalcium phosphate prepared from various phosphatic materials was dissociated with approximately 6.2 pounds of acetone/pound of P_2O_5 in MCP. The P_2O_5 yield, when similar amount of methanol was used as dissociation solvent, varied between 31.91 percent and 26.28 percent. However, P_2O_5 yield in the product acid was slightly higher, when monocalcium phosphate, prepared from each phosphatic material, was dissociated with approximately 6.2 pounds of acetone/pound of P_2O_5 in MCP than when the monocalcium phosphate prepared from the same phosphatic material was dissociated with similar amount of methanol.

The total major cation impurity (CaO, Fe_2O_3, Al_2O_3, and MgO) concentrations in the product acid were more or less identical for all

types of phosphatic materials used except in the case of Florida slimes where the Al_2O_3 content was slightly higher. It can be seen that the choice of solvent dictated which major cation impurities were preferentially rejected from the product phosphoric acid. When methanol was used as the dissociation solvent, the concentrations of Fe_2O_3 and Al_2O_3 in the product phosphoric acid were generally much lower than when acetone was the dissociation solvent. However, when acetone was used as the dissociation solvent, the concentrations of CaO and MgO were generally much lower than when methanol was the dissociation solvent. However, even though methanol rejects iron and aluminum impurities better than acetone and acetone rejects calcium and magnesium impurities better than methanol, the total major cation impurity concentration in the product phosphoric acid is approximately the same when dissociating with methanol or acetone using similar reaction conditions.

As discussed previously, the dissociation slurry filtration rate while using acetone as the dissociation solvent was much higher than when using methanol. For example, the filtration rate of the slurry resulting from the dissociation at 55°C of crude 47 percent P_2O_5 Florida monocalcium phosphate using approximately 6.2 pounds of solvent per pound of monocalcium phosphate P_2O_5 was 90 pounds of filtrate P_2O_5 per hour per square foot for acetone compared with 19 pounds of filtrate P_2O_5 per hour per square foot for methanol.

The proposed dissociation process has been shown to be capable of producing phosphoric acid of much greater purity than that from current commerical wet-acid processes, and alternatively or simultaneously producing fertilizer grade dicalcium phosphate. The phosphoric acid can

be made directly of high concentration without vacuum evaporation. The process is adaptable to use of low grade as well as high grade phosphate rocks, and of low grade phosphatic materials such as matrix or waste materials.

Production of Phosphoric Acid by Direct Acidulation of Phosphate Rock with Sulfuric Acid

A number of exploratory experimental runs were made to investigate the direct acidulation of phosphate rock with sulfuric acid or oleum and subsequent extraction of the digested mass with methanol or acetone. The data resulting from these experiments were used to evaluate the relative merits of sulfuric acid or oleum of different concentrations.

During the course of the exploratory laboratory work, it was found that acidulation of phosphate rock with strong sulfuric acid gave a slimy nonfilterable calcium sulfate from which phosphoric acid could not be extracted in a reasonable time. However, if the reaction product was heated it was possible to obtain a filterable material which was easily extracted with acetone or methanol to produce strong phosphoric acid.

In the exploratory work, dried phosphate rock containing 34.28% P_2O_5 and ground to 70 percent through 200 mesh was used. The sulfuric acid used was 98% technical grade.

The laboratory procedure consisted of heating the sulfuric acid to about 100°C and intimately mixing it with the phosphate rock for about 2 min. The product from this mixing consisted of stiff particles of about 1/8 to 3/4 in. The mixture was then heated for about 30 min

at 250°C, after which it became hard and porous. The dried acidulate was then cooled in a dessicator to a temperature of 50°C and was immediately extracted in fixed bed filters. Three stages of extraction were needed (see Appendix D) in the filtration system with 9 minutes of contact time in each of the three extraction stages. After each extraction stage the acidulate was washed with 30 ml of solvent at ambient temperature.

The data which resulted from these exploratory experimental runs are presented in Tables 11 and 12. Table 11 shows, at various concentrations of sulfuric acid, the P_2O_5 yield, the P_2O_5 concentration and percent impurity in the product acid along with the filtration rate of the extracted acid which resulted from the stagewise extraction of dried acidulate, which was prepared from Florida phosphate concentrate I, with a solvent ratio of 2 pounds of methanol in each stage/lb of P_2O_5 in dried acidulate. Table 12 persents analogous data for phosphoric acid produced by stagewise extraction of dried acidulate with acetone. These tables also show the percent total P_2O_5 in dried acidulate used in these experiments. A nearly constant ratio of approximately 2 pounds of solvent in each stage per pound of total P_2O_5 in the dried acidulate was used in the extraction stages.

The major cation impurity concentrations in the product phosphoric acid that appear in Tables 11 and 12 are shown in Tables 13 and 14 along with the major cation impurity concentrations of the product phosphoric acid on the basis of 54% P_2O_5. Tables 13 and 14 also show percent H_2SO_4 in sulfuric acid, percent total P_2O_5 in acidulate and percent P_2O_5 in product acid.

It can be seen from Tables 11 and 12 that the concentration of P_2O_5 in product phosphoric acid increased with increasing concentration

Table 11. Production of Phosphoric Acid by Stagewise Extraction of Dried Acidulate with 2 Pounds of Methanol/Pound of P_2O_5 in Dried Acidulate in Each Stage. (The Crude Acidulate were Prepared from Florida Phosphate Concentrate I and Sulfuric Acid of Different Concentrations).

H_2SO_4 in Sulfuric Acid Percent	Total P_2O_5 in Acidulate Percent	P_2O_5 Yield in Product Acid[a], Percent	Concentration of P_2O_5 in Product Acid, Percent	Percent Impurity in Product Acid					Filtration Rate, lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	F	
93.10	17.93	74.67	61.23	1.18	0.81	1.10	0.37	0.52	107;109;93[b]
98.00	18.38	95.85	66.98	1.38	0.92	1.12	0.35	0.58	102;103;100[b]
103.30	20.98	93.74	67.41	1.40	0.91	1.07	0.40	0.46	93;86;90[b]
104.50	22.09	95.73	68.25	1.47	0.88	1.04	0.40	0.60	80;76;72[b]
106.75	23.04	89.00	69.53	1.58	1.14	1.26	0.49	0.42	70;60;62[b]

a "P_2O_5 Yield" Percent P_2O_5 in the rock recovered.

b The numbers represent the filtration rate for each stage for those experimental runs made using not more than 9 mins of contact time per stage.

Table 12. Production of Phosphoric Acid by Stagewise Extraction of Dried Acidulate with 2 Pounds of Acetone/Pound of P_2O_5 in Dried Acidulate in Each Stage. (The Crude Acidulate were Prepared from Florida Phosphate Concentrate I and Sulfuric Acid of Different Concentrations).

H_2SO_4 in Sulfuric Acid Percent	Total P_2O_5 in Acidulate Percent	P_2O_5 Yield in Product Acid[a], Percent	Concentration of P_2O_5 in Product Acid, Percent	Percent Impurity in Product Acid					Filtration Rate, Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	F	
93.10	17.93	78.32	61.06	0.75	1.11	1.30	0.10	0.90	170;176;168[b]
98.00	18.38	95.26	67.01	0.82	1.19	1.33	0.14	0.98	158;151;150[b]
103.30	20.98	94.83	67.56	0.84	1.24	1.36	0.11	0.86	150;149;146[b]
104.50	22.09	94.51	68.35	0.80	1.27	1.30	0.12	0.71	138;140;136[b]
106.75	23.04	80.25	69.49	0.89	1.34	1.46	0.16	0.72	110;115;114[b]

a "P_2O_5 Yield" Percent P_2O_5 in the rock recovered.

b The numbers represent the filtration rate for each stage for those experimental runs made using not more than 9 mins of contact time per stage.

of sulfuric acid. This steady increase can be attributed to the fact that with increasing concentration of sulfuric acid, less water is introduced in the system. It may also be seen from Tables 11 and 12 that percent P_2O_5 recovery from the rock remained somewhat constant between 95-96% when the concentration of sulfuric acid was increased from 98 to 104.50. Lower P_2O_5 recovery from the rock was realized when the percent H_2SO_4 in sulfuric acid used was 106.75. This is attributable to poor mixing of the rock and the acid in the acidulation step thus rendering lesser amount of P_2O_5 in rock water soluble.

Methanol Solvent. The effect of sulfuric acid concentration on product acid P_2O_5 yield, percent P_2O_5 in product acid, product acid impurity concentration and filtration rate when methanol was used as the extraction solvent are shown in Table 11.

The P_2O_5 yield in the phosphoric acid product resulting from the stagewise extraction with 2 pounds of methanol in each stage per pound of acidulate P_2O_5 increased with increasing H_2SO_4 concentration up to 104.5% H_2SO_4 and then with further increase in H_2SO_4 concentration to 106.75% H_2SO_4, the value of P_2O_5 yield decreased. The P_2O_5 concentration in product phosphoric acid increased with increasing concentration of sulfuric acid. The total major cation impurity content of the product phosphoric acid steadily increased with increasing percent H_2SO_4 in sulfuric acid. The filtration rate of the extract decreased with increase in sulfuric acid concentration.

The effect of percent H_2SO_4 in sulfuric acid on percent impurity in product acid and percent impurity in product acid on the basis of 54 percent P_2O_5 is shown in Table 13. While the total major cation

Table 13. P_2O_5 Concentration, Impurity Concentrations in the Product Phosphoric acid and Phosphoric Acid Containing 54% P_2O_5 from Stagewise Extraction of Dried Acidulate with 2 Pounds of Methanol/Pound of P_2O_5 in Dried Acidulate in Each Stage. (The Crude Acidulates were Prepared from Florida Phosphate Concentrate I and Sulfuric Acid of Different Concentrations).

Percent H_2SO_4 in Sulfuric Acid	Percent Total P_2O_5 in Acidulate	Percent Impurity in Product Acid					Percent P_2O_5 in Product Acid	Percent Impurity in Product Acid (Basis 54% P_2O_5)				
		CaO	Fe_2O_3	AL_2O_3	MgO	Total Major cations		CaO	Fe_2O_3	Al_2O_3	MgO	Total Major cations
93.10	17.93	1.28	0.81	1.10	0.37	3.56	61.23	1.13	0.71	0.97	0.33	3.14
98.00	18.38	1.38	0.92	1.12	0.35	3.77	66.98	1.11	0.74	0.90	0.28	3.03
103.30	20.98	1.40	0.91	1.07	0.40	3.78	67.41	1.12	0.73	0.86	0.32	3.03
104.50	22.09	1.47	0.88	1.04	0.40	3.79	68.25	1.16	0.70	0.82	0.32	3.00
106.75	23.04	1.58	1.14	1.26	0.49	4.47	69.53	1.23	0.86	0.98	0.38	3.45

impurity content of the product phosphoric acid steadily increased with increasing sulfuric acid concentration the total major cation impurity content of the product phosphoric acid on the basis of 54 percent P_2O_5 remained constant with increasing H_2SO_4 concentration up to 104.50% H_2SO_4 and then with further increase in H_2SO_4 concentration to 106.75% H_2SO_4, the value increased sharply.

These results are presented graphically in Figure 3. The P_2O_5 yield in the product acid resulting from the stagewise extraction of crude Florida acidulate increased rapidly with increasing percent H_2SO_4 in sulfuric acid up to approximately 104.50 percent H_2SO_4 in sulfuric acid. As the percent H_2SO_4 in sulfuric acid was increased above 104.50, the P_2O_5 yield dropped.

Figure 3 also shows the percent P_2O_5 in product acid resulting from the stagewise extraction of crude acidulate prepared from Florida concentrate I with 2 pounds of methanol in each stage per pound of total P_2O_5 in acidulate. From the results shown, it can be seen that there is a steady increase in percent P_2O_5 in product acid with increasing percent H_2SO_4 in sulfuric acid.

Figure 3 shows the total major cation impurity (CaO, Fe_2O_3, Al_2O_3, and MgO) concentration at different concentrations of sulfuric acid in product phosphoric acid resulting from the stagewise extraction with methanol of crude acidulate prepared from Florida concentrate I. Also shown in Figure 3 is the total major cation impurity concentration in product phosphoric acid containing 54 percent P_2O_5. With increase in percent H_2SO_4 in sulfuric acid, the total major cation impurity content in the product acid steadily increased up to approximately 104.50

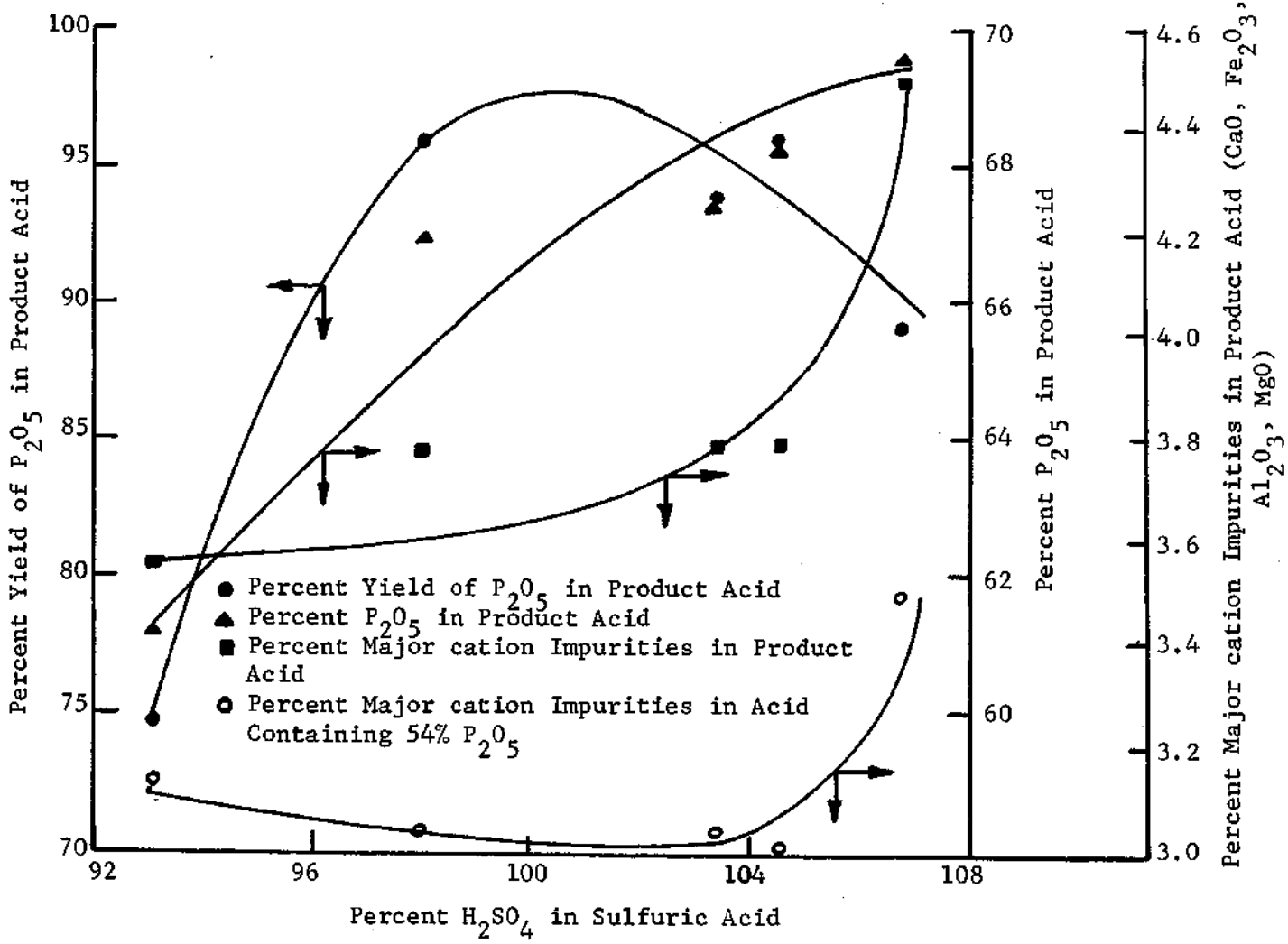

Figure 3. P_2O_5 Yield, P_2O_5 Concentration, Impurity Concentration as a Function of % H_2SO_4 in Sulfuric Acid when Acidulate is Extracted with Methanol

percent H_2SO_4 in sulfuric acid. As the percent H_2SO_4 in sulfuric acid was increased above 104.50, the increase in total major cation content in the product acid was rather sharp. The total major cation impurity content in the product acid on the basis of 54 percent P_2O_5 remained somewhat constant with increasing percent H_2SO_4 in sulfuric acid up to a value of 104.50 percent H_2SO_4 in sulfuric acid. As the percent H_2SO_4 in sulfuric acid was increased, the impurity content increased sharply.

Acetone Solvent. The effect of percent H_2SO_4 in sulfuric acid on product acid P_2O_5 yield, percent P_2O_5 in product acid, product acid impurity concentration and filtration rate when acetone was used as the extraction solvent is shown in Table 12.

With increasing concentration of sulfuric acid, the P_2O_5 yield in the product phosphoric acid resulting from the stagewise extraction with 2 pound of acetone in each stage per pound of acidulate P_2O_5 increased. The subsequent increase in concentration of sulfuric acid resulted in a somewhat constant value of P_2O_5 yield in the product acid.

The data presented in Tables 12 and 14 are also summarized in Figure 4. The percent P_2O_5 in product acid resulting from the stagewise extraction of crude acidulate prepared from Florida concentrate I increased steadily with increasing percent H_2SO_4 in sulfuric acid.

Figure 4 also shows the total major cation impurity (CaO, Fe_2O_3, Al_2O_3 and MgO) concentration at different percents H_2SO_4 in sulfuric acid in product phosphoric acid resulting from the stagewise extraction with acetone of crude acidulate prepared from Florida concentrate I. Also shown in Figure 4 is the total major cation impurity concentration in product phosphoric acid containing 54 percent P_2O_5. With increasing

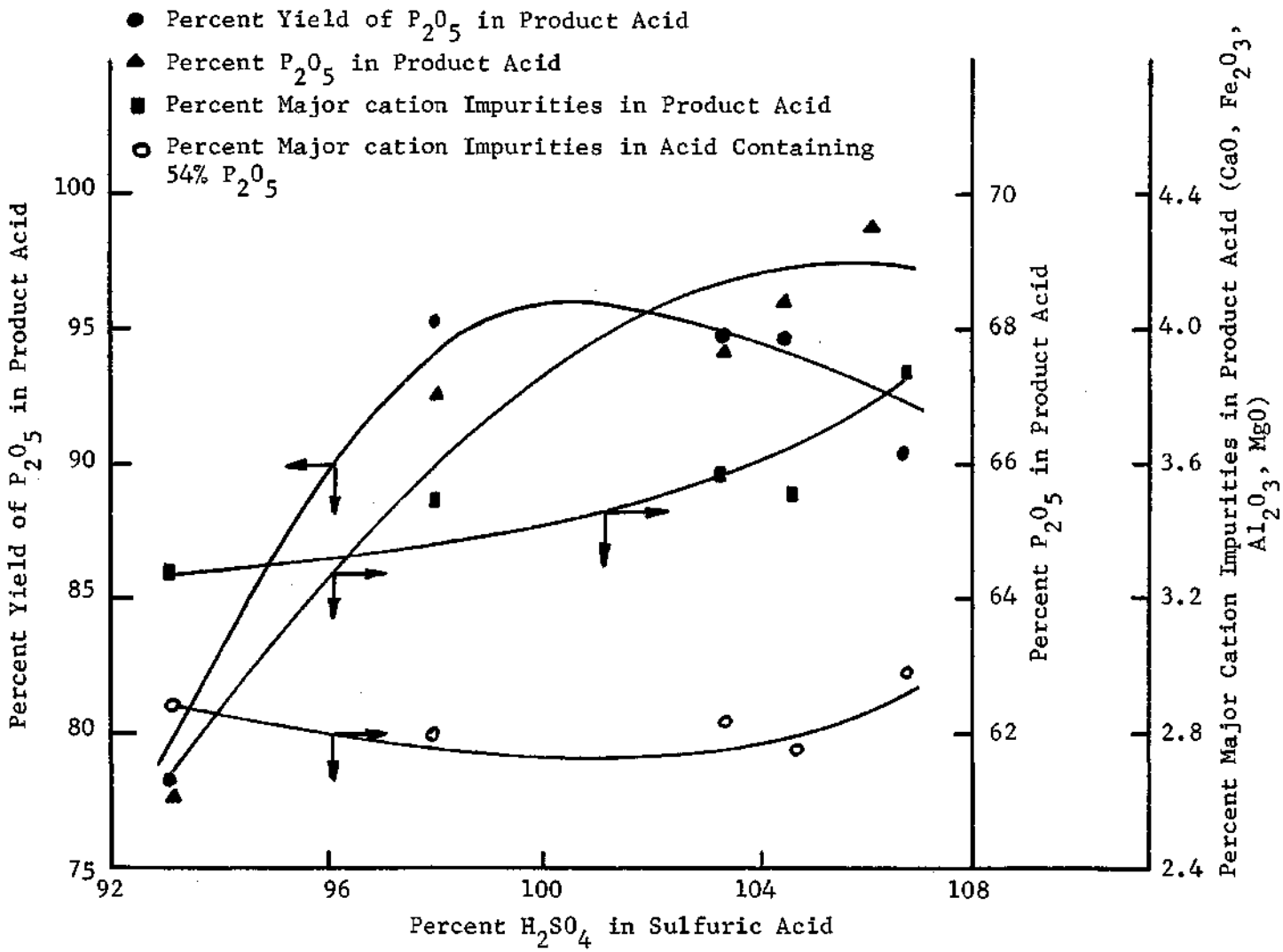

Figure 4. P_2O_5 Yield, P_2O_5 Concentration, Impurity Concentration as a Function of % H_2SO_4 in Sulfuric Acid when Acidulate is Extracted with Acetone

Table 14. P_2O_5 Concentration, Impurity Concentrations in the Product Phosphoric Acid and Phosphoric Acid Containing 54% P_2O_5 from Stagewise Extraction of Dried Acidulate with 2 Pounds of Acetone/Pound of P_2O_5 in Dried Acidulate in Each Stage. (The Crude Acidulates were Prepared from Florida Phosphate Concentrate I and Sulfuric Acid of Different Concentrations).

Percent H_2SO_4 in Sulfuric Acid	Percent Total P_2O_5 in Acidulate	Percent Impurity in Product Acid					Percent P_2O_5 in Product Acid	Percent Impurity in Product Acid (Basis 54% P_2O_5)				
		CaO	Fe_2O_3	Al_2O_3	MgO	Total Major cations		CaO	Fe_2O_3	Al_2O_3	MgO	Total Major cations
93.10	17.93	0.75	1.11	1.30	0.10	3.26	61.06	0.66	0.98	1.15	0.09	2.88
98.00	18.38	0.82	1.19	1.33	0.14	3.48	67.01	0.66	0.96	1.07	0.11	2.80
103.30	20.98	0.84	1.24	1.36	0.11	3.55	67.56	0.67	0.99	1.09	0.09	2.84
104.50	22.09	0.80	1.27	1.30	0.12	3.49	68.35	0.63	1.00	1.03	0.09	2.75
106.75	23.04	0.89	1.34	1.46	0.16	3.85	69.49	0.69	1.04	1.13	0.12	2.98

concentration of sulfuric acid, the total major cation impurity content in the product acid steadily increased up to approximately 104.50 percent H_2SO_4 in sulfuric acid. As the percent H_2SO_4 in sulfuric acid was increased above 104.50, the increase in total major cation content in the product acid was rather sharp. The total major cation impurity content in the product acid on the basis of 54 percent P_2O_5 remained constant with increasing H_2SO_4 concentration up to 104.50% H_2SO_4, and then with further increase in H_2SO_4 concentration to 106.75% H_2SO_4, the value increased sharply.

When the data concerned with the product acid impurity concentrations when using methanol solvent (see Table 13) are compared with those using acetone solvent (see Table 14), it can be seen that the choice of solvent dictated which major cation impurities were preferentially rejected from the product acid. When methanol was used as the extraction solvent, the concentrations of Fe_2O_3 and Al_2O_3 in the product phosphoric acid were generally lower than when acetone was the extraction solvent. However, when acetone was used as the extraction solvent, the concentration of CaO and MgO were generally much lower than when methanol was the extraction solvent. However, even though methanol rejects iron and aluminum impurities better and acetone rejects calcium and magnesium impurities better, the total major cation impurity concentration in the product phosphoric acid was slightly higher when methanol was used as the extraction solvent.

When the data concerned with the extracted slurry filtration rates when using methanol solvent (see Table 11) are compared with those using acetone solvent (see Table 12), it can be seen that the choice of

solvent dictated the filtration rate of the extract. When methanol was used as the extraction solvent, the filtration rate was lower than when acetone was the extraction solvent.

Near Optimum Process Conditions

Processing conditions for a chemical process are optimized in order to produce a desired product at the lowest production cost. The process associated with the production of low impurity phosphoric acid by the chemical route involving the dissociation of monocalcium phosphate in the presence of an organic solvent has already been optimized by Drees (11). The process involving the direct acidulation of phosphate rock with sulfuric acid followed by extraction of phosphoric acid with methanol and acetone produces a phosphoric acid which is intermediate in impurity content between commercial wet process phosphoric acid and commerical furnace grade phosphoric acid. During optimization, the lowest processing cost per unit of product is determined. The low impurity phosphoric acid resulting from the process might be expected to have a price intermediate between commercial wet process and commercial furnace grade phosphoric acids since its impurity content is lower than that of wet process acid, but higher than that of furnace acid. The present marketing prices (8) for tank car quantities of wet process phosphoric and furnace grade phosphoric acids containing 54 percent P_2O_5 are approximately \$68 per ton and \$152 per ton respectively. It may be seen that there exists a reasonably large difference between the prices of the two grades of phosphoric acid so that the low impurity acid could probably be successfully sold at an intermediate value to pay for any increased production cost

above that for wet process acid.

Since the prices of sulfuric acid containing different percent of H_2SO_4 are somewhat similar, the choice of sulfuric acid for digesting phosphate concentrate was made on the basis of total P_2O_5 yield in the product acid and also the total major cation impurity content of the product acid containing 54 percent P_2O_5. As can be seen from Tables 11 and 12 the sulfuric acid containing 98, 103.30, and 104.50 percent H_2SO_4 when reacted with Florida phosphate concentrate and subsequently extracted with either acetone or methanol gave the best P_2O_5 yield in the product acid. Tables 13 and 14 show that the total major cation impurity content of the product acid containing 54 percent P_2O_5 decreased with the increasing sulfuric acid concentration. The lowest value of the impurity content of the product acid on the basis of 54 percent P_2O_5 was obtained when sulfuric acid containing 104.50 percent H_2SO_4 was used for digesting the Florida phosphate concentrate and the acidulate thus produced was subsequently extracted with either acetone or methanol. However, at this point, it should be mentioned that the choice of the type of sulfuric acid would be dictated by the concentration of P_2O_5 in the product acid desired. The use of sulfuric acid, containing either 103.30 or 104.50 or 106.75 percent H_2SO_4, eliminates the heating step that is required between the acidulation and extraction stage when the sulfuric acid containing either 93.1 or 98 percent H_2SO_4 is used in the digestion of phosphate concentrate. Thus, the use of sulfuric acid containing either 103.30 or 104.50 percent H_2SO_4 would result in a substantial saving in the heating cost.

The choice of organic solvent used in the extraction of phosphoric

acid from the acidulate was made on the following basis. Methanol and acetone are the cheapest of all the solvents considered with methanol being cheaper than acetone (Table 2). Both methanol and acetone are relatively low boiling solvents which will facilitate solvent stripping from the extracted filtrate with the use of low quality heat.

The data indicate that no more than 2 minutes of reaction time is required when using sulfuric acid or fuming sulfuric acid. The acidulated mass thus produced is then either dried or held in an insulated container for a maximum period of one hour, following which, depending on the type of cooling system used, the hot acidulate is cooled to a temperature of slightly less than the normal boiling point of the solvent to be used for the subsequent extraction step. The cooled acidulated mass is then extracted with the desired solvent in three stages of 9 minutes of contact time (see Appendix D) per stage. Further work should be initiated to study the effect of different solvent/P_2O_5 ratios in the extraction of phosphoric acid from the acidulate.

Methanol is a cheaper solvent, on a weight basis, than acetone. Methanol is less volatile and, consequently, lower losses attributed to solvent vaporization would probably result with the use of methanol solvent in the process.

The use of acetone as the extraction solvent results in an extraction slurry which filters much more rapidly than that corresponding to the use of methanol resulting in a lower capital cost required for filtration equipment. Because the boiling point of acetone is lower than that of methanol, easier rectification of solvent and acid product should result in a fractionator when acetone solvent is used. Also, the use of lower

pressure steam for fractionation and filter cake drying should result when acetone is used. Since the enthalpy of vaporization of acetone is approximately one-half that of methanol, on a weight basis, the use of acetone would require much less energy for solvent fractionation and cake drying per pound of solvent used.

In general, at equal solvent/P_2O_5 ratio and equal extraction time per stage, methanol and acetone produce approximately the same filtrate P_2O_5 yield and the same P_2O_5 concentration in the product acid. The total major cation impurity concentrations in the product phosphoric acid is slightly higher when the dried acidulate is extracted with methanol than with acetone. Again, the use of methanol results in preferential rejection of iron and aluminum impurities whereas the use of acetone results in the preferential rejection of calcium and magnesium impurities.

Production of Phosphoric Acid by Direct Acidulation of Phosphatic Materials with Sulfuric Acid and Subsequent Extraction of the Acid with Methanol and Acetone Solvents

A number of exploratory experimental runs were made to investigate the direct aciduation of five different phosphatic materials with sulfuric acid containing 98 percent H_2SO_4 and subsequent extraction in the presence of acetone and methanol solvents. The data resulting from these experiments were used to evaluate the feasibility of using this process for the manufacture of low impurity, high concentration phosphoric acid from various phosphatic materials.

The data which resulted from these exploratory experimental runs are presented in Tables 15 and 16. Tables 15 and 16 show the P_2O_5 yield,

Table 15. Production of Phosphoric Acid by Stagewise Extraction of Dried Acidulate with 2 Pounds of Methanol/Pound of P_2O_5 in Dried Acidulate in Each Stage. (The Crude Acidulates were Prepared from Various Grades of Phosphatic Materials and Sulfuric Acid Containing 98 Percent H_2SO_4. Three Extraction Stages were Used for the Experiments).

Raw Material	Total P_2O_5 in Acidulate, Percent	P_2O_5 Yield in Product Acid[a], Percent	Concentration of P_2O_5 in Product Acid, Percent	Percent Impurity in Product Acid					Filtration Rate, Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	F	
N. Carolina Concentrate I	17.72	96.73	67.25	1.21	0.84	0.96	0.38	0.62	109;115;101[b]
Florida Matrix I	14.83	95.34	67.06	1.26	0.81	0.97	0.29	0.35	128;120;118[b]
Florida Matrix II	12.27	95.04	66.45	1.19	0.92	1.01	0.36	0.23	90;86;85[b]
Florida Slime	11.68	95.17	67.07	1.29	1.01	1.07	0.31	0.46	70;65;63[b]
Soft Phosphate Rock with Colloidal Clay	14.57	96.15	66.71	1.31	0.93	0.95	0.54	0.56	72;70;64[b]

a "P_2O_5 Yield" Percent P_2O_5 in the phosphatic materials recovered.

b The numbers represent the filtration rate for each stage for those experimental runs made using not more than 9 mins of contact time per stage.

Table 16. Production of Phosphoric Acid by Stagewise Extraction of Dried Acidulate with 2 Pounds of Acetone/Pound of P_2O_5 in Dried Acidulate in Each Stage. (The Crude Acidulates were Prepared from Various Grades of Phosphatic Materials and Sulfuric Acid Containing 98 Percent H_2SO_4. Three Extraction Stages were Used for the Experiments).

Raw Material	Total P_2O_5 in Acidulate, Percent	P_2O_5 Yield in Product Acid[a], Percent	Concentration of P_2O_5 in Product Acid, Percent	Percent Impurity in Product Acid					Filtration Rate, Lbs of Filtration P_2O_5 /Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	F	
N. Carolina Concentrate I	17.72	95.27	66.83	0.82	1.13	1.20	0.09	0.63	160;155;150[b]
Florida Matrix I	14.83	96.81	67.21	0.91	1.13	1.25	0.06	0.61	150;150;146[b]
Florida Matrix II	12.27	94.23	67.19	0.86	1.20	1.16	0.13	0.71	140;138;130[b]
Florida Slime	11.68	93.14	67.03	0.79	1.24	1.26	0.11	0.68	120;115;110[b]
Soft Phosphate Rock with Colloidal Clay	14.57	95.13	66.84	0.87	1.17	1.21	0.12	0.71	132;130;128[b]

a "P_2O_5 Yield" Percent P_2O_5 in the phosphatic materials recovered.

b The numbers represent the filtration rate for each stage for those experimental runs made using not more than 9 mins of contact time per stage.

P_2O_5 concentration and impurity concentration in the product phosphoric acid along with the filtration rate of the extracted phosphoric acid which resulted from the stagewise extraction of the acidulated mass, prepared from various phosphatic material, with methanol and acetone respectively. Tables 15 and 16 also show the type of phosphatic materials and the total percent P_2O_5 in the acidulated mass. Sulfuric acid used for the digestion of the phosphatic materials contained 98.00 percent H_2SO_4. A nearly constant ratio of approximately 6 pounds of solvent per pound of total P_2O_5 in the acidulated mass, being equally divided among three stages, was used for these experiments.

The cumulative percent P_2O_5 yield that appear in Tables 15 and 16 represent the percent P_2O_5 in the phosphatic materials that is recovered as product phosphoric acid. The concentrations of impurities that appear in Tables 15 and 16 represent the weight percentage of these species in product phosphoric acid that resulted from the direct acidulation of phosphatic materials with sulfuric acid containing 98 percent H_2SO_4 and subsequent extraction of the dried acidulate with either methanol or acetone. The filtration rates appearing in Tables 15 and 16 are for each stage of those experimental runs made using not more than 9 minutes of contact time per stage.

From the results given in Tables 15 and 16 it may be seen that the P_2O_5 yields of the acids produced varied from 95.04 percent to 96.73 percent when dried acidulate, prepared from various phosphatic materials, was extracted with methanol. The P_2O_5 yield, when similar amount of acetone was used as extraction solvent, varied between 93.14 percent and 96.81 percent.

The impurity concentrations in the product acid were more or less identical for all types of phosphatic materials used. It can be seen that the choice of solvent dictated which major impurities were preferentially rejected from the product phosphoric acid. When methanol was used as the dissociation solvent, the concentrations of Fe_2O_3 and Al_2O_3 in the product phosphoric acid were generally lower than when acetone was the extraction solvent. However, when acetone was used as the extraction solvent, the concentrations of CaO and MgO were generally lower than when methanol was the extraction solvent.

The filtration rate of the extract while using acetone as the extraction solvent was much higher than when using methanol.

The proposed new process has been shown to be capable of producing phosphoric acid of high concentration without vacuum evaporation. The process is adaptable to use of low grade as well as high grade phosphate rocks, and of low grade phosphatic materials such as matrix or waste materials.

CHAPTER IV

CHEMICAL PROCESS FLOW DIAGRAMS

Figure 5 shows the flow diagram for the production of low impurity phosphoric acid produced by the direct digestion of the Florida phosphate concentrate with sulfuric acid and subsequently subjecting the acidulated mass to stagewise extraction with either methanol or acetone. The flow diagram is presented along with the total mass flow rates and the compositions of the main flow streams for each process variation based on a total production of 1000 tons per day of product P_2O_5.

It should be stated at this point that the processing conditions used in the material balance for the flow sheet presented below are based on data presently available and are not necessarily optimum. The data need to be subjected to an extensive economic study in order to establish true optimum processing conditions.

The list of assumptions used in calculating the material balance are given here. The process produces 1000 tons per day of product P_2O_5 resulting from the stagewise extraction of dried acidulate produced from the direct acidulation of Florida phosphate concentrate with sulfuric acid containing 98 percent H_2SO_4. The chemical analysis of the ground phosphate concentrate reactant is as follows: 34 percent P_2O_5, 50 percent CaO, 1.3 percent Fe_2O_3, 1.3 percent Al_3O_3, 0.3 percent MgO and 3.8 percent F. Solvent losses and impurities in the recycled solvent are assumed neglibible. When using methanol, a solvent/dried acidulate

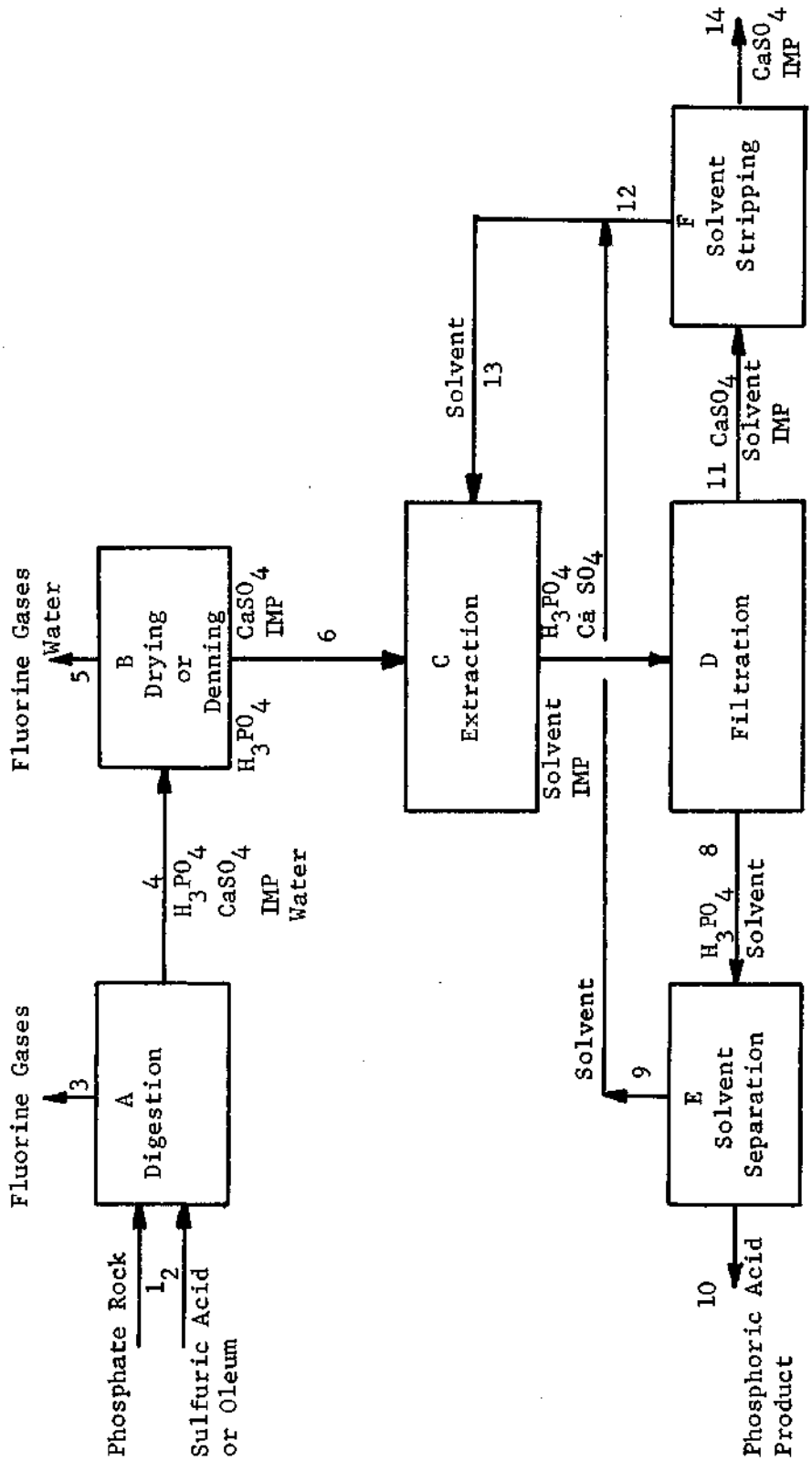

Figure 5. Schematic Diagram for the Direct Acidulation Process

P_2O_5 ratio of 6.0 tons of methanol per ton of P_2O_5, being equally divided among three stages, results in a 96 percent filtrate P_2O_5 yield during extraction. The filtration rate of the extracted phosphoric acid is 100 pounds of filtrate P_2O_5 per hour per square foot. Chemical analysis of the phosphoric acid which results after fractionation of the methanol is as follows: 67.0 percent P_2O_5, 1.38 percent CaO, 0.92 percent Fe_2O_3, 1.12 percent Al_2O_3, 0.35 percent MgO, 0.58 percent F and negligible percent sulfate. The solvent content of the wet extracted filter cake is 0.4 tons of methanol per ton of wet filter cake. When using acetone, a solvent/dried acidulate P_2O_5 ratio of 6.0 tons of acetone per ton of P_2O_5, begin equally divided among three stages, results in a 95 percent filtrate P_2O_5 yield during extraction. The filtration rate of the extracted phosphoric acid is 150 pounds of filtrate P_2O_5 per hour per square foot. Chemical analysis of the acid which results after fractionation of the acetone is as follows: 67.0 percent P_2O_5, 0.82 percent CaO, 1.19 percent Fe_2O_3, 1.33 percent Al_2O_3, 0.14 percent MgO, 0.98 percent F and negligible percent sulfate. The solvent content of the wet extracted filter cake is 0.35 tons of acetone per ton of wet filter cake.

A flow diagram showing the major processing steps and the major flow streams in the process when producing low impurity phosphoric acid is presented in Figure 5. This figure shows the chief constituents in the streams entering and leaving each of the major processing steps. Each flow stream is labeled with a number to facilitate cross-reference with Tables 17 and 18. Total mass flow rates and compositions of the main process flow streams when producing low impurity phosphoric acid (1000 tons per day of product P_2O_5 output) by extraction with 6.0 tons of

Table 17. Process Flow Rates for the Production of Low Impurity Phosphoric Acid Product Produced by Direct Acidulation of Phosphate Concentrate with Sulfuric Acid Containing 98 Percent H_2SO_4 and Subsequent Extraction of Acidulated Mass with Methanol. (The process produces 1000 tons per day of product P_2O_5. Three percent P_2O_5 losses in the waste $CaSO_4$ stream are assumed while producing the crude phosphoric acid solvent losses and impurities in the recycled solvent are assumed negligible. The solvent content of the wet filter cake is assumed to be 0.4 tons of methanol per ton of wet filter cake).

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	SO_4	Fe_2O_3	Al_2O_3	MgO	F	Solvent
1.	Phosphate Concentrate	3064	1042	1532	0	39.8	39.8	9.2	116.4	0
2.	98% Sulfuric Acid	2643	0	0	2590	0.0	0.0	0.0	0.0	0
3.	Digestor Effluent	76	0	0	0	0.0	0.0	0.0	76.0	0
4.	Acidulate Mass	5707	1042	1532	2590	39.8	39.8	9.2	40.4	0
5.	Dryer Effluent	37	0	0	0	0.0	0.0	0.0	29.0	0
6.	Dried Acidulate Mass	5670	1042	1532	2590	39.8	39.8	9.2	11.4	0
7.	Extraction Mass	11922	1042	1532	2590	39.8	39.8	9.2	11.4	6252
8.	Extracted Acid	4961	1000	20.6	0	13.7	16.7	5.3	8.6	3468
9.	Fractionated Solvent	3468	0	0	0	0.0	0.0	0.0	0.0	3468
10.	Low Impurity Acid	1493	1000	20.6	0	13.7	16.7	5.3	8.6	0
11.	Extracted Filter Cake	6961	42	1511.4	2590	26.1	23.1	3.9	2.8	2784

Table 17. (Continued)

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	SO_4	Fe_2O_3	Al_2O_3	MgO	F	Solvent
12.	Stripped Solvent	2784	0	0	0	0.0	0.0	0.0	0.0	2784
13.	Extraction Solvent	6252	0	0	0	0.0	0.0	0.0	0.0	6252
14.	Dried Calcium Sulfate	4177	42	1511.4	2590	26.1	23.1	3.9	2.8	0

Table 18. Process Flow Rates for the Production of Low Impurity Phosphoric Acid Product Produced by Direct Acidulation of Phosphate Concentrate with Sulfuric Acid Containing 98 Percent H_2SO_4 and Subsequent Extraction of Acidulated Mass with Acetone. (The process produces 1000 tons per day of product P_2O_5. Three percent P_2O_5 losses in the waste $CaSO_4$ stream are assumed while producing the crude phosphoric acid. Solvent losses and impurities in the recycled solvent are assumed negligible. The solvent content of the wet filter cake is assumed to be 0.35 tons of acetone per ton of wet filter cake).

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	SO_4	Fe_2O_3	Al_2O_3	MgO	F	Solvent
1.	Phosphate Concentrate	3097	1053	1549	0	40.3	40.3	9.3	117.7	0
2.	98% Sulfuric Acid	2672	0	0	2619	0.0	0.0	0.0	0.0	0
3.	Digestor Effluent	77	0	0	0	0.0	0.0	0.0	77.0	0
4.	Acidulate Mass	5769	1053	1549	2619	40.3	40.3	9.3	40.7	0
5.	Dryer Effluent	32	0	0	0	0.0	0.0	0.0	25.0	0
6.	Dried Acidulate Mass	5737	1053	1549	2619	40.3	40.3	9.3	15.7	0
7.	Extraction Mass	12055	1053	1549	2619	40.3	40.3	9.3	15.7	6318
8.	Extracted Acid	5526	1000	12.2	0	17.7	19.8	2.1	14.6	4033
9.	Fractionated Solvent	4033	0	0	0	0.0	0.0	0.0	0.0	4033
10.	Low Impurity Acid	1493	1000	12.2	0	17.7	19.8	2.1	14.6	0
11.	Extracted Filter Cake	6529	53	1536.8	2619	22.6	20.5	7.2	0.9	2285

Table 18. (Continued)

Process Stream	Process Stream Description	Mass Flow Rate, Tons Per Day	Constituent Flow Rate, Tons Per Day							
			P_2O_5	CaO	SO_4	Fe_2O_3	Al_2O_3	MgO	F	Solvent
12.	Stripped Solvent	2285	0	0	0	0.0	0.0	0.0	0.0	2285
13.	Extraction Solvent	6318	0	0	0	0.0	0.0	0.0	0.0	6318
14.	Dried Calcium Sulfate	4244	53	1536.8	2619	22.6	20.5	7.2	0.9	0

methanol per ton of P_2O_5 in dried acidulate, being equally divided among three stages, are shown in Table 17 while the total mass flow rates and compositions of the main process flow streams when producing low impurity phosphoric acid (1000 tons per day of product P_2O_5 output) by extraction with 6.0 tons of acetone per ton of P_2O_5 in dried acidulate are shown in Table 18.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusion

Dissociation Process

The conclusions drawn from the results obtained in the further study of the process for the production of low impurity phosphoric acid by a method involving the dissociation in the presence of an organic solvent of crude monocalcium phosphate prepared from wet process phosphoric acid and phosphatic materials, are summarized as follows:

Effect of Repeated Treatment of Monocalcium Phosphate on Dissociation Reaction. The effect of repeated treatment of monocalcium phosphate with methanol and acetone was studied by subjecting the insoluble residue from a dissociation reaction to repeated treatment with fresh solvent. From the results obtained, the cumulative % P_2O_5 yield in the product phosphoric acid increases with each subsequent treatment through three stages. The maximum conversion was about 90% of theoretical. Higher total yields were obtained with solid than with slurry monocalcium phosphate.

Product Phosphoric Acids. It is significant that the product phosphoric acid from the treatment of monocalcium phosphate containing 47% P_2O_5 had a concentration of 54.4% P_2O_5, which corresponds to commercial grade phosphoric acid, and that this concentration was achieved directly from the dissociation step after removal of the solvent and without further concentration.

The impurity contents of the product phosphoric acids made from Florida phosphate rock and North Carolina phosphate rock are significantly lower than those of present commerical acids.

Use of Low Grade Phosphatic Materials. The applicability of the process to produce high purity phosphoric acid from low grade phosphatic materials was demonstrated by preparation of phosphoric acid from several grades of Florida and North Carolina phosphate rocks, from Florida phosphate slimes, and from Florida phosphate matrix. The compositions and yields of the acids produced were found to be almost idential for all grades of phosphate rock used, and even when phosphate slimes were used the acid produced was of about the same composition except that the Al_2O_3 content was slightly higher.

It is concluded that the dissociation process is capable of producing high purity phosphoric acid from any grade of phosphatic raw material, even reject materials such as phosphate slimes. The process is also applicable to other low grade materials such as phosphate matrix.

Direct Acidulation Process

A modification and simplification of the above phosphoric acid-dicalcium phosphate process in which only phosphoric acid of high concentration can be made directly by a chemical route involving direct digestion of phosphatic materials with sulfuric acid and subsequent extraction of dried acidulate with methanol or acetone is technically feasible. The results of the investigation on the above process may be summarized as follows:

Effect of Time on Drying of the Acidulated Mass. Experiments were

made to determine the effect of moisture content of the acidulate on its filterability. From the results obtained, it is concluded that a filterable mass is obtained when the acidulate is dried for 20-60 minutes at 250°C or held in an insulated container for 60 minutes.

Effect of Overall Contact Time on Stagewise Extraction of the Dried Acidulate. A series of experiments were conducted to determine the optimum number of extraction stages and optimum contact time per stage. Seven stages were used. Total contact time was plotted against the total yield for the extraction of phosphoric acid from the dried acidulate with either methanol or acetone. It is concluded that the optimum number of stages was three with 9 minutes of contact time per stage.

Product Phosphoric Acids. It is significant that the product phosphoric acid from the extraction of dried acidulate, prepared from Florida concentrate I and sulfuric acids of different concentrations, had a concentration between 61 and 70% P_2O_5, and that these concentrations were achieved directly from the extraction step after removal of the solvent and without further concentration. The recovery of P_2O_5 from the rock was above 90% except when the rock was digested with sulfuric acid containing 93% H_2SO_4 the yield in that case was much lower.

The impurity contents of the product phosphoric acids made from Florida concentrate I are somewhat similar to that of the commerical acid containing the same percent P_2O_5.

Use of Low Grade Phosphatic Materials. The versatility of the process to produce phosphoric acid of concentration up to 70% P_2O_5 from low grade phosphatic materials was demonstrated by preparation of phosphoric acid from Florida and North Carolina phosphate concentrates,

Florida phosphate slimes and Florida phosphate matrix. The compositions, yields and concentrations of the acid produced are found to be substantially identical for all types of phosphatic materials used.

The proposed new process has been shown to be capable of producing phosphoric acid of up to 70% P_2O_5 concentration directly without vacuum evaporation. The Process is adaptable to use of low grade as well as high grade phosphate concentrates, and of low grade phosphatic materials such as matrix or waste materials.

Recommendations

The following recommendations should be given consideration in further studies of the two processes.

1. The feasibility of producing low impurity phosphoric acid containing more than 54 percent P_2O_5 directly after solvent separation by dissociating crude monocalcium phosphate containing more than 47 percent P_2O_5 in the presence of methanol and acetone should be investigated.

2. The feasibility of using a mixture of methanol and acetone for dissociating monocalcium phosphate should be investigated. There should be a substantial increase in the impurity rejection in the product acid with good filtrate P_2O_5 yield in the product acid still occuring.

3. The range of existing data concerned with the extraction of phosphoric acid with methanol and acetone from dried acidulate, obtained from direct digestion of phosphate rock with sulfuric acid, should be extended. For example, total solvent/acidulate P_2O_5 ratios higher than 6 should be investigated when extracting the dried acidulate with either methanol or acetone. Extension of existing extraction data might reveal

conditions where near optimum yield of phosphoric acid can be obtained in lesser time.

4. A continuous pilot plant study of the different process variations for both processes should be initiated to better determine optimum operating and processing conditions.

5. A comprehensive economic evaluation of the chemical process involving direct digestion of phosphate rock with sulfuric acid of different concentrations and subsequent extraction of dried acidulate with methanol and acetone should be made. Experimental data should be used to determine which of the sulfuric acids should be used for digesting the phosphate concentrate I and to determine optimum process operating conditions of a more refined nature.

APPENDIX A

CHEMICAL COMPOSITIONS AND PARTICLE SIZE DISTRIBUTION OF DRIED MONOCALCIUM PHOSPHATE MATERIALS AND DRIED OR DENNED ACIDULATE

The experimental procedures outlined in Chapter II were used in the preparation of crude monocalcium phosphate and acidulate containing various amounts of free water. The impure monocalcium phosphate slurry and acidulate were then dried or denned so that the resultant monocalcium phosphate and acidulate material contained from 41.6 to 47.0 and 11.7 to 23.0 weight percent P_2O_5 respectively. The dried monocalcium phosphate and dried acidulate were then subjected to size reduction procedures so that the largest particles passed through U.S. standard 18 mesh and 2 mesh screens respectively. The chemical compositions and particle size distributions are shown in Tables 19 and 20 respectively.

Table 19. Chemical Composition of Dried Monocalcium Phosphate and Dried Acidulate

Material Description	Composition, Weight Percent									
	Water Soluble P_2O_5	Citrate Insoluble P_2O_5	Total P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	Free Water	Water of Crystallization plus Free Water
Dried MCP from Florida Concentrate (I)	46.11	0.18	47.00	19.91	1.62	2.09	0.56	-	0.29	6.21
Dried MCP from Florida Concentrate (II)	44.28	0.76	46.40	19.22	1.38	1.81	0.39	-	0.68	5.72
Dried MCP from Florida Concentrate (III)	43.11	1.03	45.30	18.37	1.26	1.68	0.35	-	0.93	6.03
Dried MCP from Florida Concentrate (IV)	42.05	1.28	44.60	18.81	1.42	1.77	0.37	-	0.14	4.61
Dried MCP from Florida Concentrate (V)	42.63	1.36	45.40	18.56	1.63	2.28	0.53	-	0.27	5.73
Dried MCP from Florida Pebble	42.42	0.96	44.80	17.96	2.18	2.39	0.53	-	0.03	4.36
Dried MCP from Florida Slimes	34.86	1.92	41.20	21.78	2.00	3.21	0.78	-	0.00	3.18
Dried MCP from Florida Matrix (I)	39.66	1.01	42.10	17.28	1.48	1.92	0.74	-	0.02	4.31

Table 19. (Continued)

Material Description	Composition, Weight Percent									
	Water Soluble P_2O_5	Citrate Insoluble P_2O_5	Total P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	Free Water	Water of Crystallization plus Free Water
Dried MCP from Florida Matrix (II)	35.22	1.57	40.20	16.23	2.11	1.91	0.78	-	0.00	2.41
Dried MCP from Florida Matrix (III)	35.48	1.71	40.63	16.14	3.24	2.64	0.75	-	0.13	3.54
Dried MCP from Florida Matrix (IV)	34.56	1.82	38.71	16.42	3.21	3.24	0.93	-	0.00	2.98
Dried MCP from N. Carolina Concentrate (I)	43.13	1.21	46.20	19.47	1.46	2.23	0.62	-	2.78	6.93
Dried MCP from N. Carolina Concentrate (II)	42.86	1.34	45.67	19.21	1.46	2.43	0.56	-	0.03	4.24
Dried MCP from Colloidal Phosphate Rock	38.87	1.52	41.63	17.23	2.07	1.97	0.69	-	0.00	4.97
Dried Acidulate from Acidulation of Phosphate Rock and 93.1% H_2SO_4	17.69	0.24	17.93	27.49	0.83	0.86	0.14	0.20	-	-

Table 19. (Continued)

Material Description	Composition, Weight Percent									
	Water Soluble P_2O_5	Citrate Insoluble P_2O_5	Total P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	Free Water	Water of Crystallization plus Free Water
Dried Acidulate from Acidulation of Phosphate Rock and 98% H_2SO_4	18.06	0.32	18.38	27.16	0.70	0.72	0.20	0.24	-	-
Dried Acidulate from Acidulation of Phosphate Rock and 103.3% H_2SO_4	20.21	0.77	20.98	30.93	0.97	0.92	0.26	0.27	-	-
Dried Acidulate from Acidulation of Phosphate Rock and 104.50% H_2SO_4	21.04	1.05	22.09	31.04	1.09	1.10	0.31	0.30	-	-
Dried Acidulate from Acidulation of Phosphate Rock and 106.75% H_2SO_4	19.42	3.62	23.04	31.13	1.12	1.17	0.42	0.37	-	-

Table 20. Particle Size Distribution of Dried Monocalcium Phosphate and Dried or Denned Acidulate

Material Description	Cumulative Weight Percentage of Material Retained by U.S. Standard Screen								
	2	6	12	18	28	35	50	60	100
Dried MCP from Florida Concentrate (I)	-	-	-	0.00	5.67	20.15	32.63	49.18	58.28
Dried MCP from Florida Concentrate (II)	-	-	-	0.00	7.83	18.73	38.27	45.43	60.19
Dried MCP from Florida Concentrate (III)	-	-	-	0.00	7.24	16.57	43.11	46.24	59.73
Dried MCP from Florida Concentrate (IV)	-	-	-	0.00	9.45	18.79	32.63	49.81	62.53
Dried MCP from Florida Concentrate (V)	-	-	-	0.00	6.88	19.83	36.24	50.13	64.36
Dried MCP from Florida Pebble	-	-	-	0.00	3.44	12.83	52.14	59.36	60.18
Dried MCP from Florida Slimes	-	-	-	0.00	7.82	20.07	37.11	46.17	55.24
Dried MCP from Floirda Matrix (I)	-	-	-	0.00	8.73	18.73	38.44	48.29	57.97
Dried MCP from Florida Matrix (II)	-	-	-	0.00	10.44	20.39	37.17	49.57	63.11
Dried MCP from Florida Matrix (III)	-	-	-	0.00	4.79	16.77	38.59	50.54	63.87
Dried MCP from Florida Matrix (IV)	-	-	-	0.00	5.67	17.48	39.63	52.67	60.79
Dried MCP from N. Carolina Concentrate (I)	-	-	-	0.00	7.84	16.04	40.57	48.07	59.08

Table 20. (Continued)

Material Description	Cumulative Weight Percentage of Material Retained by U.S. Standard Screen								
	2	6	12	18	28	35	50	60	100
Dried MCP from N. Carolina Concentrate (II)	-	-	-	0.00	8.33	22.99	39.37	46.52	62.14
Dried MCP from Colloidal Phosphate Rock	-	-	-	0.00	6.07	24.53	40.13	47.32	60.17
Dried Acidulate from Acidulation of Phosphate Rock and 93.1% H_2SO_4	0.00	32.43	45.67	63.54	89.53	-	-	-	-
Dried Acidulate from Acidulation of Phosphate Rock and 98% H_2SO_4	0.00	34.51	46.72	64.45	90.73	-	-	-	-
Dried Acidulate from Acidulation of Phosphate Rock and 103.30% H_2SO_4	0.01	30.16	47.73	60.11	92.45	-	-	-	-
Dried Acidulate from Acidulation of Phosphate Rock and 104.50% H_2SO_4	0.03	36.21	45.73	63.17	90.42	-	-	-	-
Dried Acidulate from Acidulation of Phosphate Rock and 106.75% H_2SO_4	0.00	32.47	50.24	60.11	87.47	-	-	-	-

APPENDIX B

EXPERIMENTAL FILTRATE P_2O_5 YIELDS, IMPURITY REJECTIONS AND FILTRATION RATES FOR STAGEWISE DISSOCIATION OF MONOCALCIUM PHOSPHATE PREPARED FROM FLORIDA PHOSPHATE ROCK IN METHANOL AND ACETONE

The experimental procedures outlined in Chapter II were used to investigate the stagewise dissociation of crude monocalcium phosphate containing approximately 32 and 47 percent P_2O_5 in the presence of acetone and methanol after different reaction time periods using different solvent/monocalcium phosphate P_2O_5 ratios in each stage. The crude monocalcium phosphate was prepared from ground Florida phosphate rock.

Tables 21 and 22 shows the P_2O_5 yields, the major cation impurity (CaO, Fe_2O_3, Al_2O_3, and MgO) concentrations in product phosphoric acid containing 54 percent total P_2O_5 resulting from the first stage of the stagewise dissociation of crude monocalcium phosphate containing 32 percent P_2O_5 in methanol and acetone respectively. The filtration rates of the slurries resulting from these dissociation experiments are also listed. A sample of dissociation slurry was vacuum filtered using water aspiration to provide the vacuum through a filtration medium of known area as described in Chapter II. By measuring the time required to filter the slurry sample until the top portion of the cake appeared dry and after analyzing the resulting filtrate P_2O_5, the filtration rate in units of pounds of filtrate P_2O_5 per hour per square foot of filtration area was then calculated. The crude monocalcium phosphate P_2O_5 concentration and

Table 21. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from First Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Methanol of Different Solvent Ratios. (The crude MCP slurry prepared from Florida phosphate rock reaction and filtration temperature was 55°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
31.86	6.30	0.25	35.21	0.68	0.11	0.20	0.71	28
		0.50	34.11	0.61	0.06	0.19	0.76	33
		0.75	33.32	0.59	0.11	0.20	0.74	31
		1.00	36.64	0.72	0.08	0.21	0.83	36

Table 22. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from First Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Acetone at Different Solvent Ratios. (The crude MCP slurry prepared from Florida phosphate rock reaction and filtration temperature was 50°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
31.86	6.42	0.25	27.83	0.15	0.10	0.26	0.17	316
		0.50	28.43	0.14	0.09	0.37	0.12	311
		0.75	28.64	0.13	0.13	0.24	0.16	300
		1.00	29.59	0.14	0.12	0.29	0.15	297
31.86	7.19	0.25	28.69	0.13	0.09	0.36	0.11	302
		0.50	29.32	0.10	0.08	0.30	0.14	289
		0.75	30.21	0.11	0.11	0.26	0.12	298
		1.00	29.86	0.14	0.12	0.28	0.15	307
31.86	8.16	0.25	28.48	0.11	0.08	0.28	0.13	301
		0.50	29.31	0.09	0.07	0.31	0.08	303
		0.75	30.32	0.14	0.12	0.22	0.10	316
		1.00	30.37	0.18	0.13	0.31	0.17	308

methanol or acetone/monocalcium phosphate P_2O_5 ratio are shown along with the dissociation reaction time for each experiment.

Tables 23 and 24 show the P_2O_5 yields, the major cation impurity (CaO, Fe_2O_3, Al_2O_3 and MgO) concentrations in product phosphoric acid containing 54 percent total P_2O_5 resulting from the second stage of the stagewise dissociation of unreacted monocalcium phosphate from the first stage using methanol and acetone respectively. The filtration rates of the slurries resulting from these dissociation experiments are also listed. The unreacted monocalcium phosphate P_2O_5 concentration and methanol or acetone/unreacted monocalcium phosphate P_2O_5 ratio are shown along with the dissociation reaction time for each experiment. The unreacted monocalcium phosphate P_2O_5 concentration shown in Tables 23 and 24 were obtained from dissociation for one hour of crude monocalcium phosphate containing 32 percent P_2O_5 with 6.30 pounds of methanol per pound of total P_2O_5 in unreacted MCP and 8.16 pounds of acetone per pound of total P_2O_5 in unreacted MCP, respectively.

Tables 25 and 26 show the P_2O_5 yields, the major cation impurity (CaO, Fe_2O_3, Al_2O_3, and MgO) concentrations in product phosphoric acid containing 54 percent total P_2O_5 resulting from the third stage of the stagewise dissociation of unreacted monocalcium phosphate from the second stage using methanol and acetone respectively. The filtration rates of the slurries resulting from these dissociation experiments are also listed. The unreacted monocalcium phosphate P_2O_5 ratio are shown along with the dissociation reaction time for each experiment. The unreacted monocalcium phosphate P_2O_5 concentration shown in Table 25 were obtained from dissociation of crude monocalcium phosphate containing 32 percent

Table 23. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from Second Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Methanol at Different Solvent Ratios. (The crude MCP slurry prepared from Florida phosphate rock reaction and filtration temperature was 55°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
28.47	3.98	0.25	4.68	0.56	0.09	0.17	0.59	30
		0.50	4.90	0.49	0.06	0.25	0.63	32
		0.75	4.71	0.53	0.07	0.20	0.66	26
		1.00	4.83	0.50	0.10	0.22	0.56	28
28.47	4.98	0.25	5.29	0.48	0.07	0.20	0.64	26
		0.50	5.31	0.43	0.09	0.22	0.59	25
		0.75	5.42	0.43	0.10	0.19	0.66	29
		1.00	5.50	0.45	0.10	0.19	0.64	28
28.47	6.02	0.25	5.72	0.40	0.06	0.22	0.58	26
		0.50	5.77	0.48	0.08	0.14	0.62	29
		0.75	5.80	0.41	0.05	0.21	0.57	30
		1.00	5.83	0.39	0.09	0.15	0.59	27
28.47	7.06	0.25	6.42	0.44	0.09	0.18	0.58	24
		0.50	6.49	0.38	0.08	0.16	0.58	27
		0.75	6.49	0.42	0.07	0.14	0.55	28
		1.00	6.52	0.40	0.08	0.20	0.57	25
28.47	8.03	0.25	6.24	0.41	0.07	0.19	0.54	27
		0.50	6.32	0.36	<0.05	0.18	0.51	28

Table 23. (Continued)

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate, P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
		0.75	6.25	0.42	0.05	0.19	0.49	24
		1.00	6.21	0.41	0.08	0.20	0.54	25

Table 24. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from Second Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Acetone at Different Solvent Ratios. (The crude MCP slurry prepared from Florida phosphate rock reaction and filtration temperature was 50°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
29.36	4.22	0.25	1.11	0.11	0.09	0.22	0.11	250
		0.50	1.17	0.10	0.08	0.34	0.14	247
		0.75	1.26	0.10	0.11	0.24	0.10	262
		1.00	1.42	0.17	0.12	0.24	0.17	265
29.36	5.16	0.25	2.16	0.12	0.10	0.24	0.14	230
		0.50	2.22	0.09	0.10	0.22	0.10	242
		0.75	2.41	0.13	0.07	0.32	0.09	256
		1.00	2.37	0.10	0.09	0.34	0.15	260
29.36	6.14	0.25	2.42	0.14	0.11	0.31	0.08	224
		0.50	2.79	0.13	0.06	0.30	0.14	223
		0.75	2.91	0.09	0.07	0.30	0.11	246
		1.00	2.83	0.12	0.12	0.25	0.19	235
29.36	7.18	0.25	3.39	0.07	0.08	0.26	0.09	240
		0.50	3.46	0.08	0.08	0.30	0.11	264
		0.75	3.61	0.12	0.10	0.27	0.14	219
		1.00	3.54	0.13	0.14	0.25	0.18	221
29.36	8.12	0.25	3.51	0.08	0.09	0.29	0.13	223
		0.50	3.72	0.09	0.13	0.28	0.13	219

Table 24. (Continued)

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
		0.75	3.86	0.11	0.11	0.28	0.10	208
		1.00	4.11	0.12	0.11	0.19	0.12	206
29.36	9.21	0.25	3.78	0.09	0.12	0.26	0.11	197
		0.50	3.97	0.10	0.09	0.26	0.08	208
		0.75	4.02	0.13	0.08	0.22	0.10	207
		1.00	4.19	0.12	0.11	0.22	0.15	212

Table 25. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from Third Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Methanol at Different Solvent Ratios. (The crude MCP slurry prepared from Florida phosphate rock reaction and filtration temperature was 55°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
26.87	4.01	0.25	0.11	0.38	0.07	0.16	0.49	>22
		0.50	0.12	0.39	0.06	0.20	0.53	>27
		0.75	0.08	0.42	<0.05	0.20	0.51	>26
		1.00	0.09	0.33	0.07	0.16	0.51	>29
26.87	5.06	0.25	0.28	0.37	<0.05	0.17	0.49	>27
		0.50	0.29	0.39	0.05	0.16	0.51	>23
		0.75	0.31	0.38	0.05	0.19	0.56	>26
		1.00	0.32	0.42	0.06	0.16	0.52	>28

Table 26. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from Third Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Acetone at Different Solvent Ratios. (The crude MCP slurry prepared from Florida phosphate rock reaction and filtration temperature was 50°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
27.23	4.16	0.25	0.68	0.12	0.11	0.20	0.13	182
		0.50	0.77	0.10	0.09	0.24	0.10	187
		0.75	0.81	0.06	0.13	0.23	0.09	206
		1.00	0.90	0.08	0.07	0.25	0.16	213
27.23	5.21	0.25	1.60	0.06	0.12	0.22	0.09	150
		0.50	1.66	0.10	0.10	0.26	0.12	146
		0.75	1.80	0.09	0.11	0.21	0.10	168
		1.00	1.90	0.11	0.11	0.27	0.13	184
27.23	6.18	0.25	2.16	0.09	0.09	0.20	0.08	140
		0.50	2.28	0.10	0.08	0.24	0.08	152
		0.75	2.36	0.06	0.12	0.22	0.12	160
		1.00	2.40	0.07	0.11	0.26	0.12	168
27.23	7.18	0.25	2.32	0.06	0.09	0.21	0.12	130
		0.50	2.44	0.09	0.08	0.25	0.09	128
		0.75	2.57	0.05	0.12	0.20	0.08	142
		1.00	2.63	0.08	0.11	0.22	0.11	144

P_2O_5 with 6.30 and 7.06 pounds of methanol per pound of total P_2O_5 in unreacted MCP in successive stages, while the unreacted monocalcium phosphate P_2O_5 concentrations shown in Table 26 were obtained from dissociation of crude monocalcium phosphate containing 32 percent P_2O_5 with 8.16 and 8.12 pounds of acetone per pound of total P_2O_5 in unreacted MCP in successive stages.

Tables 27 and 28 show the P_2O_5 yields, the major cation impurity (CaO, Fe_2O_3, Al_2O_3, and MgO) concentrations in product phosphoric acid containing 54 percent total P_2O_5 resulting from the first stage of the stagewise dissociation of crude monocalcium phosphate containing 47 percent P_2O_5 using methanol and acetone respectively. The filtration rates of the slurries resulting from these dissociation experiments are also given. The crude monocalcium phosphate P_2O_5 concentration and methanol or acetone/monocalcium phosphate P_2O_5 ratio are shown along with the dissociation reaction time for each experiment.

Tables 29 and 30 show the P_2O_5 yields, the major cation impurity (CaO, Fe_2O_3, Al_2O_3, and MgO) concentrations in product phosphoric acid containing 54 percent total P_2O_5 resulting from the second stage of the stagewise dissociation of unreacted monocalcium phosphate from the first stage using methanol and acetone respectively. The filtration rates of the slurries resulting from these dissociation experiments are also listed. The unreacted monocalcium phosphate P_2O_5 concentration and methanol or acetone/unreacted monocalcium phosphate P_2O_5 ratio are shown along with the dissociation reaction time for each experiment. The unreacted monocalcium phosphate P_2O_5 concentrations shown in Tables 29 and 30 were obtained from dissociation for one hour of crude monocalcium

Table 27. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from First Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Methanol at Different Solvent Ratios. (The crude MCP slurry prepared from Florida Phosphate rock reaction and filtration temperature was 55°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
47.00	6.19	0.25	28.93	0.49	0.06	0.12	0.13	18
		0.50	29.95	0.58	0.09	0.08	0.17	20
		0.75	30.41	0.56	0.07	0.09	0.16	26
		1.00	30.71	0.61	0.10	0.07	0.18	24
47.00	7.21	0.25	32.90	0.48	0.07	0.09	0.12	20
		0.50	33.16	0.58	0.10	0.09	0.16	21
		0.75	33.52	0.60	0.11	0.03	0.15	23
		1.00	34.12	0.58	0.08	0.11	0.13	24
47.00	8.17	0.25	33.79	0.49	0.05	0.09	0.14	19
		0.50	34.08	0.53	0.07	0.11	0.12	23
		0.75	34.36	0.53	0.07	0.07	0.18	18
		1.00	34.97	0.53	0.09	0.05	0.16	20
47.00	9.15	0.25	33.67	0.48	0.08	0.07	0.11	18
		0.50	33.98	0.49	0.09	0.08	0.12	21
		0.75	34.21	0.63	0.06	0.13	0.17	24
		1.00	34.54	0.60	0.09	0.08	0.20	21

Table 28. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from First Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Acetone at Different Solvent Ratios. (The crude MCP slurry prepared from Florida phosphate rock reaction and filtration temperature was 50°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
47.00	6.22	0.25	32.48	0.10	0.38	0.44	<0.05	90
		0.50	32.91	0.11	0.37	0.34	0.07	89
		0.75	32.98	0.06	0.32	0.41	0.05	83
		1.00	33.35	0.09	0.29	0.49	0.05	90
47.00	7.18	0.25	34.46	0.06	0.36	0.33	<0.05	80
		0.50	34.56	0.09	0.26	0.44	0.05	72
		0.75	34.68	0.08	0.33	0.49	0.07	83
		1.00	34.78	0.09	0.29	0.50	0.08	89
47.00	8.19	0.25	35.88	0.09	0.30	0.40	0.07	76
		0.50	36.11	0.09	0.33	0.35	0.05	70
		0.75	36.18	0.08	0.31	0.48	<0.05	80
		1.00	36.23	0.06	0.34	0.41	0.05	86
47.00	9.23	0.25	35.90	0.08	0.33	0.41	<0.05	72
		0.50	36.23	0.08	0.26	0.45	0.05	73
		0.75	36.56	0.07	0.31	0.39	0.07	83
		1.00	36.59	0.05	0.30	0.43	0.08	76

Table 29. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from Second Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Methanol at Different Solvent Ratios. (The crude MCP slurry prepared from Florida Phosphate rock reaction and filtration temperature was 55°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
44.32	4.17	0.25	1.68	0.58	0.06	0.09	0.13	21
		0.50	1.78	0.53	0.09	0.09	0.16	20
		0.75	2.14	0.57	0.11	0.03	0.15	18
		1.00	2.00	0.48	0.06	0.11	0.12	17
44.32	5.06	0.25	4.11	0.55	0.06	0.08	0.17	18
		0.50	4.28	0.56	0.09	0.08	0.11	19
		0.75	4.32	0.43	0.07	0.09	0.16	22
		1.00	4.49	0.54	0.06	0.11	0.16	21
44.32	6.12	0.25	5.36	0.55	0.07	0.05	0.14	21
		0.50	5.48	0.51	0.06	0.07	0.13	22
		0.75	5.63	0.54	0.07	0.10	0.16	16
		1.00	5.53	0.52	0.08	0.06	0.09	21
44.32	7.13	0.25	7.11	0.54	0.05	0.10	0.11	16
		0.50	7.36	0.52	0.06	0.07	0.10	17
		0.75	7.28	0.49	0.06	0.05	0.14	17
		1.00	7.45	0.49	0.07	0.06	0.13	22
44.32	8.16	0.25	8.39	0.46	0.05	0.07	0.12	16
		0.50	8.47	0.48	0.06	0.08	0.13	15

Table 29. (Continued)

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
		0.75	8.56	0.52	0.06	0.07	0.12	16
		1.00	8.58	0.50	0.07	0.06	0.15	26
44.32	9.14	0.25	8.82	0.44	0.04	0.09	0.09	16
		0.50	8.72	0.39	0.04	0.05	0.10	17
		0.75	8.80	0.56	0.05	0.05	0.12	20
		1.00	8.86	0.45	0.07	0.05	0.13	19
44.32	10.12	0.25	8.82	0.46	0.07	<0.05	0.09	19
		0.50	8.81	0.44	0.04	0.08	0.12	17
		0.75	8.94	0.42	0.05	0.05	0.10	20
		1.00	9.03	0.36	0.04	0.06	0.13	20

Table 30. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from Second Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Acetone at Different Solvent Ratios. (The crude MCP slurry prepared from Florida phosphate rock reaction and filtration temperature was 50°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
45.36	4.18	0.25	1.41	0.05	0.26	0.45	<0.05	60
		0.50	1.52	<0.05	0.29	0.41	0.06	67
		0.75	1.61	0.07	0.30	0.35	0.05	64
		1.00	1.54	0.08	0.27	0.35	0.05	73
45.36	5.21	0.25	2.78	0.08	0.28	0.38	0.05	58
		0.50	2.89	<0.05	0.21	0.44	0.06	60
		0.75	3.06	0.07	0.23	0.36	<0.05	64
		1.00	3.07	0.05	0.32	0.26	0.05	66
45.36	6.18	0.25	3.86	0.06	0.29	0.36	<0.05	68
		0.50	4.03	0.06	0.22	0.40	0.06	69
		0.75	3.97	<0.05	0.24	0.36	0.06	63
		1.00	4.22	<0.05	0.33	0.28	<0.05	72
45.36	7.21	0.25	5.76	0.05	0.32	0.27	0.05	72
		0.50	5.77	0.06	0.25	0.38	0.05	68
		0.75	5.89	0.07	0.28	0.38	0.06	63
		1.00	5.82	0.06	0.23	0.33	<0.05	61
45.36	8.15	0.25	6.66	0.06	0.22	0.47	0.05	62
		0.50	6.81	<0.05	0.27	0.37	0.05	58

Table 30. (Continued)

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
		0.75	6.83	0.06	0.26	0.30	0.06	59
		1.00	6.98	<0.05	0.29	0.30	<0.05	61
45.36	9.21	0.25	7.72	0.05	0.22	0.38	0.06	60
		0.50	7.84	0.05	0.28	0.38	0.06	53
		0.75	7.89	0.05	0.24	0.37	<0.05	52
		1.00	7.95	0.05	0.26	0.39	<0.05	59
45.36	10.12	0.25	7.99	0.05	0.22	0.40	0.05	53
		0.50	8.11	-	0.26	0.35	0.05	51
		0.75	8.13	-	0.25	0.38	0.05	48
		1.00	8.21	0.05	0.27	0.27	0.05	52
45.36	11.22	0.25	8.10	<0.05	0.22	0.37	<0.05	47
		0.50	8.21	0.06	0.23	0.29	<0.05	51
		0.75	8.23	-	0.27	0.29	0.06	51
		1.00	8.34	-	0.24	0.37	0.06	43

phosphate containing 47 percent P_2O_5 with 8.17 pounds of methanol per pound of total P_2O_5 in unreacted MCP and 8.19 pounds of acetone per pound of total P_2O_5 in unreacted MCP respectively.

Tables 31 and 32 show the P_2O_5 yields, the major cation impurity (CaO, Fe_2O_3, Al_2O_3, and MgO) concentrations in product phosphoric acid containing 54 percent total P_2O_5 resulting from the third stage of the stagewise dissociation of unreacted monocalcium phosphate from the second stage using methanol and acetone respectively. The filtration rates of the slurries resulting from these dissociation experiments are also listed. The unreacted monocalcium phosphate P_2O_5 ratios are shown along with the dissociation reaction time for each experiment. The unreacted monocalcium phosphate P_2O_5 concentration shown in Table 31 were obtained from dissociation of crude monocalcium phosphate containing 47 percent P_2O_5 with 8.17 and 9.14 pounds of methanol per pound of total P_2O_5 in unreacted MCP in successive stages, while the unreacted monocalcium phosphate P_2O_5 concentration shown in Table 32 were obtained from dissociation of crude monocalcium phosphate containing 47 percent P_2O_5 with 8.19 and 10.12 pounds of acetone per pound of total P_2O_5 in unreacted MCP in successive stages.

In order to facilitate comparison of the data, the filtrate P_2O_5 yields, the product acid impurity concentrations and filtration rates for stagewise dissociation of crude monocalcium phosphate containing 32 percent P_2O_5 in methanol and acetone are presented in Tables 5 and 7 respectively. Similarly the data for stagewise dissociation of crude monocalcium phosphate containing 47 percent P_2O_5 in methanol and acetone are presented in Tables 6 and 8 respectively. The values of the filtrate

Table 31. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from Third Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Methanol at Different Solvent Ratios. (The crude MCP slurry prepared from Florida phosphate rock reaction and filtration temperature was 50°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
41.06	4.06	0.25	0.92	0.42	<0.05	0.05	0.10	16
		0.50	0.98	0.40	0.05	<0.05	0.07	19
		0.75	0.99	0.36	<0.05	<0.05	0.07	17
		1.00	1.11	0.42	0.06	0.05	0.12	20
41.06	5.12	0.25	1.42	0.36	<0.05	0.09	0.09	16
		0.50	1.48	0.43	<0.05	<0.04	0.10	15
		0.75	1.56	0.38	<0.05	0.05	0.08	23
		1.00	1.54	0.39	-	-	0.13	26
41.06	6.16	0.25	1.49	0.33	0.05	<0.05	0.07	16
		0.50	1.60	0.39	<0.05	<0.05	0.08	18
		0.75	1.57	0.36	<0.05	<0.05	0.08	19
		1.00	1.58	0.44	-	-	0.09	15

Table 32. Variation of P_2O_5 Yield, Impurity Concentration and Filtration Rate for Phosphoric Acid from Third Stage in Stagewise Dissociation of Crude Monocalcium Phosphate with Acetone at Different Solvent Ratios. (The crude MCP slurry prepared from Florida phosphate rock reaction and filtration temperature was 50°C).

Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid in Stage, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate, Lbs of Filtrate P_2O_5/Hr/Sq Ft of Filtration Area
				CaO	Fe_2O_3	Al_2O_3	MgO	
41.71	4.18	0.25	0.62	-	0.24	0.32	0.05	39
		0.50	0.61	-	0.24	0.30	0.05	38
		0.75	0.56	-	0.20	0.31	0.05	31
		1.00	0.57	0.05	0.20	0.31	0.05	36
41.71	5.12	0.25	1.18	-	0.22	0.34	<0.05	31
		0.50	1.20	0.05	0.26	0.29	<0.05	33
		0.75	1.23	-	0.23	0.29	0.06	32
		1.00	1.23	-	0.25	0.28	0.06	32
41.71	6.21	0.25	1.49	-	0.22	0.40	0.06	27
		0.50	1.59	-	0.23	0.38	<0.05	26
		0.75	1.63	0.05	0.29	0.28	<0.05	32
		1.00	1.69	0.05	0.26	0.30	0.06	27

P_2O_5 yields, product acid impurity concentrations and filtration rates, shown in Table 5, 6, 7, and 8 are after one hour of dissociation reaction time periods in each stage.

APPENDIX C

EXPERIMENTAL FILTRATE P_2O_5 YIELDS, IMPURITY REJECTIONS AND FILTRATION RATES FOR DISSOCIATION OF MONOCALCIUM PHOSPHATE PREPARED FROM VARIOUS GRADE OF PHOSPHATIC MATERIALS IN METHANOL AND ACETONE

The experimental procedures outlined in Chapter II were used to investigate the dissociation of crude monocalcium phosphate, prepared from various grades of phosphatic materials, in the presence of methanol and acetone after different reaction time periods. Solvent/monocalcium phosphate P_2O_5 ratios of approximately 6.2 were used during experimentation.

Table 33 shows the filtrate P_2O_5 yields major cation impurity (CaO, Fe_2O_3, Al_2O_3, and MgO) concentrations in product phosphoric acid containing 54 percent P_2O_5 resulting from the dissociation in the presence of methanol and acetone of crude monocalcium phosphate prepared from various grades of phosphatic materials. Table 33 also gives the filtration rates of the slurries resulting from these dissociation experiments. A sample of dissociation slurry was vacuum filtered using water aspiration to provide the vacuum through a filtration medium of known area as described in Chapter II. By measuring the time required to filter the slurry sample until the top portion of the cake appeared dry and after analyzing the resulting filtrate for P_2O_5, the filtration rate in units of pounds of filtrate P_2O_5 per hour per square foot of filtration area was then calculated. The crude monocalcium phosphate

Table 33. Variation of P_2O_5 Yield Impurity Concentration and Filtration Rate with Reaction time for Phosphoric Acid from the Dissociation of Crude Monocalcium Phosphate Using Methanol and Acetone. (The crude MCP were prepared from various grades of phosphatic materials. Reaction and filtration temperatures for acetone and methanol were 50°C and 55°C respectively).

Raw Materials ($\%P_2O_5$)	Solvent	Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
						CaO	Fe_2O_3	Al_2O_3	MgO	
Florida Concentrate (I) (34.3)	Methanol	47.00	6.19	0.25	28.93	0.49	0.06	0.12	0.13	18
				0.50	29.95	0.58	0.09	0.08	0.17	20
				0.75	30.41	0.56	0.07	0.09	0.16	26
				1.00	30.71	0.61	0.10	0.07	0.18	24
	Acetone	47.00	6.22	0.25	32.48	0.10	0.38	0.44	0.03	90
				0.50	32.91	0.11	0.37	0.34	0.07	89
				0.75	32.98	0.06	0.32	0.41	0.05	83
				1.00	32.93	0.09	0.29	0.49	0.05	90
Florida Concentrate (II) (34.2)	Methanol	46.40	6.21	0.25	27.85	0.41	0.08	0.10	0.19	33
				0.50	28.11	0.40	0.11	0.07	0.22	38
				0.75	28.31	0.47	0.10	0.13	0.23	35
				1.00	28.52	0.48	0.07	0.14	0.20	34
	Acetone	46.40	6.18	0.25	28.79	0.06	0.40	0.48	0.08	69
				0.50	29.13	0.09	0.42	0.55	0.07	70
				0.75	29.39	0.08	0.47	0.44	0.11	64
				1.00	29.89	0.05	0.47	0.49	0.14	77

Table 33. (Continued)

Raw Materials ($\%P_2O_5$)	Solvent	Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
						CaO	Fe_2O_3	Al_2O_3	MgO	
Florida Concentrate (III) (33.5)	Methanol	45.30	6.18	0.25	27.76	0.43	0.06	0.08	0.28	29
				0.50	27.99	0.40	0.06	0.11	0.31	32
				0.75	28.28	0.48	0.11	0.10	0.33	31
				1.00	28.37	0.45	0.13	0.07	0.32	30
	Acetone	45.30	6.23	0.25	28.97	0.07	0.37	0.44	0.06	57
				0.50	29.49	0.07	0.75	0.61	0.09	58
				0.75	29.36	0.11	0.61	0.57	0.05	75
				1.00	29.78	0.07	0.39	0.50	0.08	52
Florida Concentrate (IV) (33.0)	Methanol	44.60	6.24	0.25	27.91	0.39	0.07	0.17	0.22	22
				0.50	28.69	0.40	0.08	0.11	0.26	20
				0.75	28.39	0.44	0.14	0.07	0.23	24
				1.00	28.21	0.49	0.07	0.09	0.25	21
	Acetone	44.60	6.19	0.25	28.87	0.06	0.47	0.45	0.06	59
				0.50	29.31	0.06	0.69	0.78	0.08	56
				0.75	29.22	0.09	0.61	0.41	0.08	73
				1.00	29.40	0.07	0.35	0.48	0.06	65
Florida Concentrate (V) (32.3)	Methanol	45.40	6.21	0.25	27.91	0.45	0.15	0.07	0.23	22
				0.50	28.36	0.50	0.15	0.09	0.24	20
				0.75	28.49	0.49	0.09	0.10	0.21	21
				1.00	28.04	0.51	0.06	0.10	0.24	19

Table 33. (Continued)

Raw Materials ($\%P_2O_5$)	Solvent	Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
						CaO	Fe_2O_3	Al_2O_3	MgO	
	Acetone	45.40	6.19	0.25	29.86	0.07	0.38	0.52	0.04	57
				0.50	30.12	0.08	0.39	0.36	0.04	65
				0.75	30.28	0.08	0.40	0.41	0.04	51
				1.00	30.54	0.09	0.47	0.39	0.04	51
Florida Pebble (28.9)	Methanol	44.80	6.23	0.25	27.31	0.44	0.08	0.12	0.30	15
				0.50	27.86	0.47	0.09	0.09	0.31	15
				0.75	28.21	0.49	0.12	0.14	0.28	17
				1.00	28.22	0.44	0.15	0.17	0.35	19
	Acetone	44.80	6.21	0.25	28.86	0.06	0.46	0.76	0.06	49
				0.50	29.09	0.06	0.48	0.60	0.06	46
				0.75	29.31	0.09	0.47	0.55	0.06	53
				1.00	29.14	0.11	0.63	0.57	0.06	48
Florida Matrix I (20.2)	Methanol	42.10	6.14	0.25	26.11	0.59	0.12	0.14	0.64	11
				0.50	26.89	0.62	0.18	0.21	0.54	11
				0.75	26.97	0.53	0.26	0.17	0.61	10
				1.00	27.23	0.54	0.16	0.12	0.69	11
	Acetone	42.10	6.18	0.25	29.21	0.06	0.28	0.41	0.06	50
				0.50	29.32	0.06	0.36	0.44	0.08	52
				0.75	29.26	0.07	0.32	0.35	0.08	49
				1.00	29.41	0.09	0.28	0.36	0.06	56

Table 33. (Continued)

Raw Materials (% P_2O_5)	Solvent	Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
						CaO	Fe_2O_3	Al_2O_3	MgO	
Florida Matrix II (15.8)	Methanol	40.20	6.20	0.25	26.56	0.59	0.27	0.30	0.56	9
				0.50	26.89	0.56	0.26	0.31	0.54	9
				0.75	26.72	0.69	0.28	0.33	0.61	9
				1.00	26.87	0.60	0.23	0.16	0.61	9
	Acetone	40.20	6.15	0.25	27.93	0.08	0.53	0.41	0.06	43
				0.50	28.31	0.10	0.43	0.47	0.06	36
				0.75	28.48	0.09	0.23	0.52	0.06	39
				1.00	28.88	0.09	0.29	0.32	0.06	33
Florida Matrix III (11.8)	Methanol	40.63	6.13	0.25	27.80	0.46	0.28	0.29	0.61	9
				0.50	27.14	0.40	0.27	0.29	0.71	8
				0.75	27.24	0.63	0.27	0.27	0.67	8
				1.00	27.42	0.51	0.42	0.43	0.77	9
	Acetone	40.63	6.09	0.25	27.41	0.08	0.37	0.55	0.07	30
				0.50	27.46	0.09	0.41	0.62	0.06	24
				0.75	27.36	0.09	0.56	0.57	0.07	25
				1.00	28.17	0.10	0.34	0.70	0.08	28
Florida Matrix IV (7.5)	Methanol	38.71	6.21	0.25	26.17	0.58	0.36	0.32	0.60	7
				0.50	26.34	0.62	0.23	0.37	0.52	7
				0.75	26.41	0.61	0.32	0.42	0.59	7
				1.00	26.28	0.63	0.41	0.25	0.53	8

Table 33. (Continued)

Raw Materials ($\%P_2O_5$)	Solvent	Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
						CaO	Fe_2O_3	Al_2O_3	MgO	
	Acetone	38.71	6.14	0.25	28.36	0.07	0.35	0.44	0.14	27
				0.50	28.49	0.07	0.37	0.35	0.09	25
				0.75	28.61	0.07	0.41	0.33	0.10	26
				1.00	28.54	0.07	0.39	0.27	0.11	27
Soft Phosphate Rock with Colloidal Clay (20.4)	Methanol	41.63	6.13	0.25	26.91	0.66	0.35	0.33	0.36	9
				0.50	27.21	0.76	0.27	0.29	0.30	10
				0.75	27.28	0.72	0.29	0.34	0.30	9
				1.00	27.40	0.82	0.33	0.48	0.28	9
	Acetone	41.63	6.08	0.25	28.42	0.12	0.39	0.46	0.07	31
				0.50	28.77	0.11	0.39	0.45	0.05	26
				0.75	28.88	0.14	0.52	0.53	0.11	31
				1.00	28.73	0.15	0.42	0.48	0.09	25
Florida Slime (14.3)	Methanol	41.20	6.20	0.25	26.89	0.49	0.20	0.89	0.41	10
				0.50	27.11	0.52	0.23	0.90	0.36	10
				0.75	27.52	0.52	0.22	0.92	0.37	11
				1.00	28.08	0.51	0.19	0.93	0.50	10
	Acetone	41.20	6.26	0.25	29.86	0.05	0.59	1.04	0.05	50
				0.50	30.24	0.06	0.60	1.24	0.05	51
				0.75	30.11	0.06	0.64	1.15	0.05	58
				1.00	30.59	0.07	0.61	1.41	0.05	61

Table 33. (Continued)

Raw Materials ($\%P_2O_5$)	Solvent	Percent Total P_2O_5 in Unreacted MCP	Pounds of Solvent Per Pound of Total P_2O_5 in Unreacted MCP	Reaction Time, Hours	P_2O_5 Yield in Product Acid, Percent	Percent Impurity in Product Acid Containing 54 Percent P_2O_5				Filtration Rate Lbs of Filtrate P_2O_5 /Hr/Sq Ft of Filtration Area
						CaO	Fe_2O_3	Al_2O_3	MgO	
North Carolina Concentrate I (32.9)	Methanol	46.20	6.28	0.25	29.79	0.60	0.08	0.28	0.65	21
				0.50	30.61	0.68	0.09	0.31	0.62	21
				0.75	30.89	0.62	0.07	0.34	0.60	27
				1.00	31.91	0.66	0.12	0.23	0.57	24P
	Acetone	46.20	6.26	0.25	31.78	0.04	0.60	0.30	0.12	88
				0.50	31.96	0.06	0.64	0.27	0.11	83
				0.75	32.13	0.06	0.61	0.35	0.11	80
				1.00	32.53	0.04	0.63	0.32	0.10	90
North Carolina Concentrate II (30.6)	Methanol	45.67	6.20	0.25	28.58	0.51	0.06	0.05	0.10	19
				0.50	29.21	0.48	0.07	0.06	0.11	18
				0.75	29.76	0.61	0.08	0.06	0.12	19
				1.00	30.85	0.64	0.11	0.07	0.11	21
	Acetone	45.67	6.23	0.25	30.81	0.07	0.26	0.35	0.06	83
				0.50	31.11	0.07	0.27	0.34	0.06	84
				0.75	31.31	0.09	0.30	0.24	0.06	78
				1.00	31.57	0.09	0.29	0.31	0.06	80

P_2O_5 concentration and methanol and acetone/monocalcium phosphate P_2O_5 ratios are shown along with the dissociation reaction time for each experiment.

In order to facilitate comparison of the data, the filtrate P_2O_5 yields, the product acid impurity concentrations and filtration rates after one hour of dissociation reaction time period are presented in Table 10.

APPENDIX D

EXPERIMENTAL FILTRATE P_2O_5 YIELD IN THE STAGEWISE EXTRACTION OF PHOSPHORIC ACID FROM DRIED ACIDULATE OBTAINED FROM DIRECT ACIDULATION OF PHOSPHATE CONCENTRATE WITH SULFURIC ACID

The experimental procedures outlined in Chapter II were used to investigate the stagewise extraction of dried acidulate containing approximately 19 percent P_2O_5 in the presence of acetone or methanol after different overall contact time divided equally in each stage and using a solvent/dried acidulate P_2O_5 ratio of 2 in each stage of extraction. The dried acidulate was prepared from ground Florida phosphate concentrate.

Table 34 shows the type of solvent, number of extraction stages, total overall contact time and also contact time for each stage and overall percent recovery of P_2O_5. Extraction was carried out in 4 in. diameter and 2 in. deep Buchner funnel. A Hoffman clamp was used to pinch the polyethylene tube, attached to the stem of the funnel, so that the organic solvent could be held in contact with the acidulate for a desired period of time. The filtrate collected, after the solvent has been in contact with the acidulate, was analyzed and percent P_2O_5 recovery was subsequently calculated.

The results given in Table 34 are summaried in Figure 6. The total P_2O_5 yield in the product acid resulting from the stagewise extraction of dried acidulate containing 19 percent P_2O_5 increased rapidly with increasing overall contact time up to 36 minutes. As the overall

Table 34. Variation of P_2O_5 Yield in the Stagewise Extraction of Phosphoric Acid from Dried Acidulate with Either Acetone or Methanol at Different Overall Contact Time and a Ratio of Solvent/Dried Acidulate of 2 in Each Stage of Extraction. (The Dried Acidulate Containing 19 Percent P_2O_5 was Prepared from Florida Phosphate Concentrate).

Types of Solvent	Number of Stages	Contact Time, Mins. per Stage	Contact Time, Mins. Total	Percent Overall Recovery of P_2O_5 in Filtrate
Acetone	7	1	7	63.78
Methanol	7	1	7	59.72
Acetone	7	2	14	74.51
Methanol	7	2	14	69.87
Acetone	6	3	18	80.53
Methanol	6	3	18	84.74
Acetone	5	4	20	88.37
Methanol	5	4	20	87.76
Acetone	5	5	25	94.59
Methanol	5	5	25	94.08
Acetone	4	10	40	98.18
Methanol	4	10	40	96.91
Acetone	4	15	60	96.26
Methanol	4	15	60	97.22
Acetone	4	20	80	96.53
Methanol	4	20	80	98.04
Acetone	4	25	100	95.79
Methanol	4	25	100	96.94
Acetone	4	30	120	98.42
Methanol	4	30	120	98.33

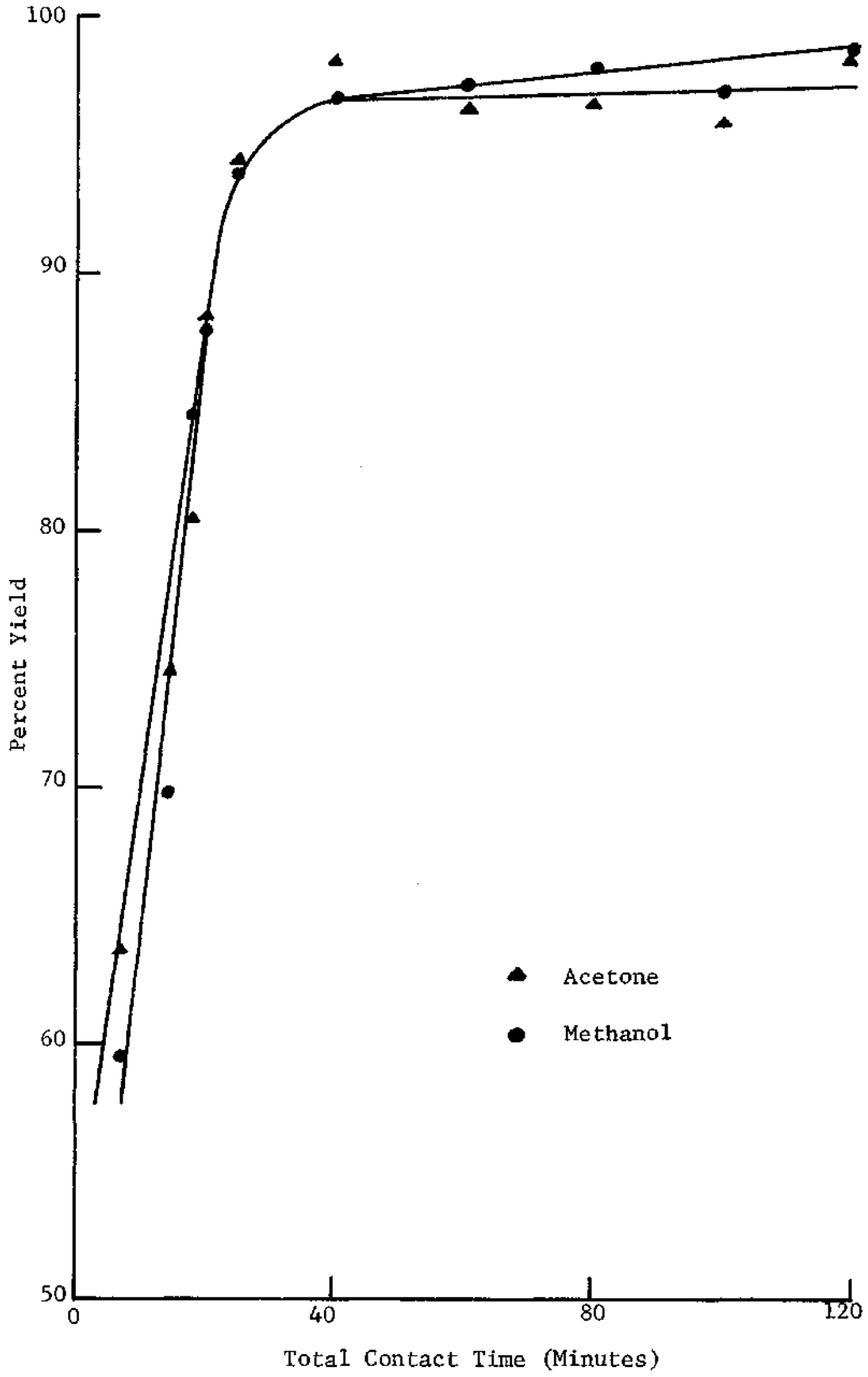

Figure 6. P_2O_5 Yield as a Function of Total Contact Time When Acidulate is Extracted with Acetone or Methanol

contact time was increased above 36 minutes the product phosphoric acid yield became relatively constant at approximately 97 percent. From Fig. 6 it can be seen that the P_2O_5 yield in product phosphoric acid when extracted with either methanol or acetone increased at the same rate with increasing overall contact time up to 25 minutes. As the overall contact time was increased above 25 minutes, the product phosphoric acid yield was slightly higher when extracted with methanol than with acetone.

It can be seen from Fig. 6 that when extracting the dried acidulate with either methanol or acetone, an optimum yield of approximately 97 percent P_2O_5 in product phosphoric acid resulted when the overall contact time was 36 minutes. Hence, four extraction stages with 9 minutes of contact time per stage seems to be sufficient.

Three and four extraction stages with 9 minutes of contact time per stage were carried out with both acetone and methanol. The dried acidulate containing approximately 19 percent P_2O_5 was obtained from direct acidulation of Florida phosphate concentrate and 98% sulfuric acid. The results are as follows:

Type of Solvent	Number of Stages	Contact time, per Stage	Mins Total	Percent Overall Recovery of P_2O_5
Acetone	3	9	27	96.43
Methanol	3	9	27	96.21
Acetone	4	9	36	97.01
Methanol	4	9	36	97.57

From the above results, it is apparent that 3 stages of extraction with 9 mins. of contact time per stage are sufficient.

APPENDIX E

SAMPLE CALCULATION

The sample calculations listed below are the same as those given by Drees (11):

1. Digestion of ground phosphate rock or dissociation filter cake residue with sulfuric acid,

2. Preparation of monocalcium phosphate from phosphate rock and phosphoric acid,

3. Dissociation filtrate P_2O_5 yield and impurity concentrations in low impurity phosphoric acid,

4. Dissociation slurry filtration rates,

5. Dissociation residue hydration state.

The following sample calculation is given in order to clarify computational procedures used in this work.

Direct Acidulation of Ground Phosphate Rock with Sulfuric Acid

Reactants used in acidulation were ground Florida phosphate rock containing 34.28 percent P_2O_5 and 49.50 percent CaO, technical grade sulfuric acid containing 98 percent H_2SO_4. For computational purposes, it was assumed that a wet process acid would be produced that contained 67.0 percent P_2O_5 and 2.0 percent free sulfuric acid. It was also assumed that 96.5 percent of the phosphate in the ground phosphate rock would be digested by the sulfuric acid leaving the remaining 3.5 percent of the P_2O_5 undigested in the by-product calcium sulfate. It

was also assumed that all the calcium oxide in the ground phosphate rock would be converted to calcium sulfate anhydrite.

A basis of 100.00 grams of ground phosphate rock reactant is used in the following calculation:

$$(100.00 \text{ gm} \cdot \text{rock})\left(0.3428 \frac{\text{gm } P_2O_5}{\text{gm} \cdot \text{rock}}\right)\left(0.965 \frac{\text{gm} \cdot P_2O_5 \text{ digested}}{\text{gm} \cdot P_2O_5 \text{ in rock}}\right)$$

$$= 33.08 \text{ gm} \cdot P_2O_5 \text{ digested.}$$

$$\frac{33.08 \text{ gm} \cdot P_2O_5 \text{ digested}}{0.67 \text{ gm} \cdot P_2O_5/\text{gm} \cdot \text{phosphoric acid}} = 49.37 \text{ gm} \cdot \text{phosphoric acid.}$$

$$(49.37 \text{ gm} \cdot \text{phosphoric acid})\left(0.02 \frac{\text{gm} \cdot \text{sulfuric acid}}{\text{gm} \cdot \text{phosphoric acid}}\right)$$

$$= 0.99 \text{ gm} \cdot \text{free sulfuric acid in phosphoric acid.}$$

$$(100.0 \text{ gm} \cdot \text{rock})\left(0.4950 \frac{\text{gm} \cdot \text{CaO}}{\text{gm} \cdot \text{rock}}\right) = 49.50 \text{ gm} \cdot \text{CaO or } 0.8827 \text{ gm} \cdot \text{mole CaO in phosphate rock}$$

$$(0.8827 \text{ gm} \cdot \text{mole CaO in rock})\left(0.965 \frac{\text{gm} \cdot \text{CaO digested}}{\text{gm} \cdot \text{CaO in rock}}\right)$$

$$= 0.8518 \text{ gm} \cdot \text{mole CaO converted to calcium sulfate anhydrite.}$$

Since each mole of CaO requires one mole of H_2SO_4 for calcium sulfate anhydrite precipitation:

$$(0.8518 \text{ gm} \cdot \text{mole } H_2SO_4)\left(98.082 \frac{\text{gm} \cdot H_2SO_4}{\text{gm} \cdot \text{mole } H_2SO_4}\right) = 83.55 \text{ gm} \cdot H_2SO_4 \text{ required for calcium sulfate anhydrite precipitation.}$$

83.55 gm · H_2SO_4 for calcium sulfate anhydrite +0.99 gm H_2SO_4 for phosphoric acid = 84.54 gm. total H_2SO_4 required.

$$\frac{84.54 \text{ gm} \cdot H_2SO_4}{0.98 \frac{\text{gm} \cdot H_2SO_4}{\text{gm} \cdot \text{sulfuric acid}}} = 86.27 \text{ gm} \cdot \text{sulfuric acid required.}$$

To summarize, the amounts of reactants required for this reaction are as follows:

100.00 grams ground phosphate rock.

86.27 grams sulfuric acid.

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